VOL. XXI. [SEPTEMBER, 1899.] NO. 9.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN, DR. A. B. PRESCOTT, DIRECTOR.]

THE DISTINCTION OF TRUE EXTRACT OF VANILLA FROM LIQUID PREPARATIONS OF VANILLIN.

BY WILLIAM H. HESS.

Received April 29, 1899.

AN "extract of vanilla" can not be made artificially that will duplicate the one made from the bean itself, either in respect to chemical behavior, or with regard to usefulness as a flavoring agent. During the sweating process in preparing the vanilla bean for market, chemical changes of unknown nature take place, and as a result of these changes, the aroma is much improved. The importance of this process is well known, and those conditions which produce the best flavor are carefully studied.[1] To provide the various ingredients of the vanilla bean artificially and so treat them that the delicate aroma incorporated in an alcoholic tincture shall equal that acquired from the bean is a hopeless task, and it is quite as difficult to deceive the analyst by such a product. The vanillin that is synthesized and put upon the market, is identical with the vanillin extracted from the bean itself. There are other constituents as tannin, gum, and organic acids which might be duplicated, and whose origin could not be easily proved. There is one important constituent, however, which will be extremely difficult to replace, and that is the

[1] See article by Prof. H. H. Rusby, Merck's Report, Feb. 1, 1898, p. 74.

resin. This resin behaves so differently from other resins that its separation and identification is a most valuable means of proving the origin of "vanilla extract."

Vanilla beans contain from four to eleven per cent. of this resin. It is of a dark red to brown color. The coloring-matter furnished by this resin constitutes about one-half of the color of the tincture of vanilla. Since manufacturers desire a deeply colored product, they are careful to get all the resin in solution. This resin is soluble in fifty per cent. alcohol so that in the "extract" of high grade where plenty of alcohol is used, all the resin is kept in solution. In cheap extracts where as little as twenty per cent. of alcohol by volume is sometimes used, an alkali, usually potassium bicarbonate, is added to aid in getting resin, gum, etc., in solution, and also for the purpose of preventing subsequent turbidity. The color is thus deepened very materially. As vanillin is acidic in character and decomposes carbonates to form salts, the delicate flavor is impaired to a considerable extent by the addition of an alkaline carbonate, and a foreign odor is thereby introduced that is quite disagreeable and not difficult to recognize.

In testing preparations of vanilla it is well to make a pharmacopoeial tincture to be used in parallel tests, along with the sample of unknown purity. The following simple tests have been found useful:

1. DILUTION TEST.

Place a few cc. of the alcoholic tincture in a test-tube and add water slowly to three times the original volume and shake. If no alkali has been used in making the extract, a flocculent reddish brown precipitate will separate out. There should be but a slight turbidity. A milky solution would indicate foreign resin. Now add hydrochloric acid, a drop at a time, to a portion of the diluted sample. Turbidity results at once, due to extracted matter held in solution by the plant bases, as well as by alkali purposely added. The turbidity produced on acidifying should be slight (absence of foreign resin). Some practice with this simple test will enable an inspector to judge somewhat of the character of a "vanilla extract." If alkali have been used,

the turbidity increases considerably, and the *color* will fade when acid is added.

2. SEPARATION AND IDENTIFICATION OF THE RESIN.

Place 25 cc. of the "extract" to be examined in an evaporating dish and drive off the alcohol on a water-bath. When the alcohol is all gone, make up to about the original volume with water. If alkali have not been used in the manufacture of the "extract," the resin will appear as an amorphous, flocculent, red to brown residue. Acidify the cool solution with a few drops of hydrochloric acid to free the resin from bases, and the whole of the resin will separate out leaving a partly decolorized and clear supernatant liquid, after standing a short time. If it is desirous to weigh the resin for a quantitative determination, several hours are necessary for its complete separation. Collect the resin on a filter, wash with water, and reserve the filtrate for further tests.

Place a piece of the filter with the resin attached in a few cc. of dilute caustic potash. The resin dissolves to a deep red solution. On acidifying, the resin is reprecipitated.

Make a solution of the resin in alcohol. To one portion of this alcoholic tincture add a few drops of ferric chloride. No striking coloration is produced. To another portion of the alcoholic tincture add some hydrochloric acid, and again there is little change in color. Most resins give color reaction with ferric chloride or hydrochloric acid in alcoholic solution.

3. TESTS OF COLORING-MATTER.

(*a*) *For caramel.*—Concentrate a portion of the filtrate obtained from the resin in an evaporating dish on a water-bath until the depth of color is approximately that of the original tincture. Now add a few drops more of strong hydrochloric acid (nitric or dilute sulphuric acid will also serve), and heat gently. If caramel be present a yellowish red, flocculent precipitate is formed, very much resembling a precipitate of iron hydroxide in color and texture. Cool and filter out this precipitate, and wash it with water. It is insoluble in water, strong alcohol, or ether. It is soluble in dilute caustic potash, in gla-

cial acetic acid, and in dilute alcohol. About one half the color of caramel is thus removed.[1]

(*b*) *For an azo dye.*—To a small portion of the filtrate add some ammonia. With a natural product the color is very much deepened. Now add some zinc dust and let it digest. The color should not fade entirely even on heating, but the solution will assume a tint about as deep as it was before adding ammonia. If the coloring be due to an azo dye it will fade to a colorless solution, the azo being reduced to the hydrazo compound. Pour some of the decolorized product into an open dish so as to expose considerable surface of liquid to the oxygen of the air. In case an hydrazo group has been formed, it will be slowly oxidized back to the colored azo compound. The oxidation may be hastened by adding some hydrogen peroxide, and the color will return at once. Other reducing agents as stannous chloride and hydrochloric acid, will also serve.

Test a portion of the original solution from the resin for tannin. This substance is present in small quantity only, and should not be found in great excess.

To another portion of the sample add a few drops of lead acetate solution. A bulky flocculent precipitate should form, showing the presence of organic acids and extractives in considerable quantity. This test should be the first, and absence of a precipitate condemns the sample. This precipitate will carry with it nearly all the coloring-matter left in the filtrate from the resin.

Vanilla extract is frequently adulterated with the "Extract of Tonka." The sophistication is best detected by ascertaining the presence of coumarin, the odoriferous constituent of the tonka bean. For a quick method of detecting coumarin in presence of vanillin, see a previous paper from this laboratory.[2]

[1] For further tests for caramel see Author in *Ztschr. anal. Chem.* (*1885*), p. 30. The following method for caramel and resin will be found most convenient and satisfactory in examining commercial extracts. If the solution, free from alcohol, is acidified slightly with hydrochloric acid and digested a few minutes on a water-bath, both the resin and caramel will be precipitated. Now filter, wash well with water to remove all sugar, and dry the precipitate and filter-paper at a low temperature. Treat the precipitate with absolute alcohol as long as any color is washed out. This removes the resin and leaves the caramel on the filter. The alcohol may be evaporated from the resin and the latter may then be treated as above. The residue is easily proved to be caramel by dissolving it in hot dilute acetic acid and adding phenylhydrazine to the solution, when a reddish brown precipitate will form which is characteristic at this point.

[2] This Journal, **21**, 256 (*1899*); *Pharm. Review*, **17** (Jan., 1899).

This investigation has been made at the request of Prof. Albert B. Prescott, to whom I wish to express my thanks for counsel in the work.

UNIVERSITY OF MICHIGAN, April 25, 1899.

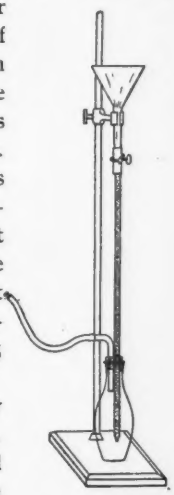
[CONTRIBUTIONS FROM THE LABORATORY OF LAFAYETTE COLLEGE.]

A SIMPLIFIED REDUCTOR.

BY P. W. SHIMER.

Received June 3, 1899.

FOR the reduction of iron and phosphomolybdate solutions, I have been using, for some time, a form of reductor which is simple, convenient, and effective. The reductor tube is a plain glass tube three-eighths inch in internal diameter and twenty inches long, drawn-out and cut off at the lower end. It is filled by placing a few small pieces of broken glass in the drawn-out portion and on this about an inch of well-cleaned sand. The tube is then filled with amalgamated zinc of as nearly uniform twenty mesh size as possible. About eighty grams are required. No asbestos or glass wool is used. The sand prevents particles of zinc from falling through, and it does not become clogged by use. Should any error arise on account of the omission of a more perfect filter, it would show in the blank, which is, however, uniformly very small, not more than 0.05 to 0.10 cc. permanganate.



The use of amalgamated zinc, as proposed by A. G. McKenna, makes a small reductor possible. The consumption of zinc is very small, and when the column has settled about one inch, a little fresh zinc can easily be poured in above. The reductor tube is united with a four-inch funnel by means of rubber tubing, well tightened with wire. Between the funnel and reductor is a Hoffman clamp. The lower end of the tube passes through a soft two-hole stopper so far as to reach half way to the bottom of a heavy-walled pint gas-bottle. The gas-bottle is connected with a filter-pump through an intermediate safety-bottle and valve. The funnel is clamped to a retort stand in such a

manner as to allow the tube and gas-bottle to swing easily in all directions. It is well to so adjust the height as to leave the gas-bottle raised slightly above the base. The passage of the solution through the reductor may be effected either by use of the pump, or by means of the vacuum obtained by condensation of steam, devised originally in Bunsen's laboratory. In using the latter method a little water may be boiled in the gas-bottle until all air is expelled and then quickly unite with the reductor, the clamp on the filter-pump tube being closed. The speed of filtration is regulated by the upper clamp. Instead of filling the gas-bottle with steam by boiling water in it, it is better to have a convenient tin or copper can containing boiling water and provided with one or more short steam outlet tubes on top. The empty gas-bottle is inverted over one of these steam outlets and, when filled with live steam, is taken off and united as quickly as possible with the reductor. This latter method has the advantage of starting with an empty gas-bottle, which is desirable, on the score of accuracy, both in iron and phosphorus determinations. When a large number of reductions have to be made, a number of reductors may be used, and, with a steam vessel provided with a number of outlets, gas-bottles may always be ready for reductions.

The hot lower part of the reductor in the gas-bottle is particularly effective in perfecting the reduction of phosphomolybdate solutions. The reduction is to $Mo_{24}O_{37}$ and the factor is 0.88163.

A few phosphorus determinations are the following:

No.	Volumetric.	Gravimetric.
1	0.041	0.041
2	0.0155	0.017
3	0.098	0.098
4	0.040	0.039

A few iron determinations in Alabama red ore are as follows: 48.52, 48.52, 48.51, 48.46, 48.52.

By reduction with five grams zinc in a flask the result on this ore was 48.45.

The speed of filtration through the reductor should not be too rapid. From three and a half to five minutes should be allowed for a reduction.

ON VAN'T HOFF'S EQUATION AND THE MOLECULAR WEIGHTS OF LIQUIDS.

By C. L. Speyers.

Received May 9, 1899.

CONSIDER the equation

$$\frac{n}{N+n} = \frac{p-p'}{p} \text{ or } \frac{n}{N} = \frac{p-p'}{p'}, \qquad (1)$$

where n is the number of gram-molecules of solute, N is the number of gram-molecules of solvent calculated from the ordinary molecular weight, that is, the molecular weight of the solvent in the solution, *not* the molecular weight of the solvent in the vapor state between pressures p and p', and p and p' are the vapor-pressures of pure solvent and solution, respectively.

Consider also the equation

$$\frac{n}{N} = l\frac{p}{p'}, \qquad (2)$$

where N is now calculated from molecular weight of the solvent in the vapor state between pressures p and p', the other letters being the same as for equation (1).

When p' is only a trifle smaller than p, then the two equations are just about equivalent, but they are not at all equivalent when p' is quite different from p. In the applications of these equations the difference $p-p'$ has hitherto been small and either equation has answered for the purposes desired. But recently the vapor-pressures of some concentrated solutions have been measured and for these solutions, equation (2) seems to fail lamentably while equation (1) seems to give excellent results.

The vapor-pressures have been measured by Noyes and Abbott,[1] by Goodwin and Burgess,[2] by Linebarger,[3] and by Lehfeldt.[4]

Noyes and Abbott, and Goodwin and Burgess, used solutions of naphthalene, azobenzene, benzophenone, and diphenylamin, in ether. The concentrations of their solutions ran up to about fourteen per cent. gram-molecules of solute.

When curves are plotted from equations (1) and (2) for which

[1] *Ztschr. phys. Chem.*, **23**, 56 (*1897*).
[2] *Ibid.*, **28**, 99 (*1899*).
[3] This Journal, **17**, 615, 690 (*1895*).
[4] *Phil. Mag.*, **46**, 42 (*1898*).

curves p' is the ordinate and the per cent. gram-molecules is the abscissa, the values obtained from each curve agree pretty well with experiment, so long as the solutions are dilute, but as the solutions grow more concentrated, the deviation from observation increases, and the deviation increases more markedly with p' calculated from (2) than with that calculated from (1). In making such comparison we must of course assign a molecular weight to the solute. I assigned a normal molecular weight to each solute. Had a different molecular weight been assigned to the solute, and I think for naphthalene at any rate we certainly ought to have done so, then the calculated values for p' could be made to agree with the observed values. So these experiments do not declare strongly against either equation. But the observations of Linebarger and of Lehfeldt will compel us to reject (2) in favor of (1). They used liquids miscible in all proportions so that we can follow the molecular weights of solvent and solute from infinite dilution to complete purity. How equation (1) is to be applied, I have tried to show.[1]

Mixtures of chlorbenzene with benzene, chlorbenzene with toluene, brombenzene with benzene, carbon tetrachloride with toluene, when plotted with vapor-pressures as ordinates and per cent. gram-molecules as abscissas, all have partial vapor-pressures so nearly straight lines that we seem compelled to go further and put them as straight lines. This means that the molecular weight of the solute does not change at all with concentration; therefore, we must assume that the molecular weight of the solute in such solutions is normal, for whenever we can follow a molecular weight that is not normal, we find that it is variable with the concentration.

If we claim that equation (1) is not applicable but that equation (2) is the correct one to use, and that the molecular weight of the solute varies in such way that (2) is possible, then we are led to absurd values for the molecular weight of the solute.

Let w be the weight of the solute, W be the weight of the solvent, m be the molecular weight of the solute, M be the molecular weight of the solvent; then,

$$n = \frac{w}{m} \text{ and } N = \frac{W}{M},$$

[1] *J. phys. Chem.*, **2**, 347 (*1898*): This Journal, **21**, 282 (*1899*).

and we have from (1)

$$m = \frac{Mw}{W} \frac{p'}{p - p'}. \qquad (3)$$

and from (2),

$$m = \frac{Mw}{W(lp - lp')}. \qquad (4)$$

Let us apply these equations to the mixture of benzene and acetic acid at 35°, using data recalculated[1] from Linebarger's experiments. The following table contains these data:

HC_2H_3O per cent. gram-molecules.	C_6H_6 per cent. gram-molecules.	V. P. $HC_2H_3O_2$ (26.5).	V. P. C_6H_6 (146).	Mol. wt. C_6H_6 by (3).	Mol. wt. C_6H_6 by (4).	Mol. wt. $HC_2H_3O_2$ by (3).	Mol. wt. $HC_2H_3O_2$ by (4).
10	90	2.8	140	78	312	156	158
30	70	8.0	127	78	152	172	184
50	50	13.2	109	78	112	177	205
70	30	18.7	85.8	78	87.7	199	263
90	10	23.8	45.0	78	84.1	241	459
93	7	24.6	34.3	78	78.9	245	550
96	4	25.2	22.5	78	63	262	770
98	2	25.9	12.6	78	68.7	278	1200

The molecular weight of benzene is not absurd as calculated by either formula, though suspiciously low by formula (4) in solutions dilute with respect to benzene. The molecular weight of acetic acid keeps within acceptable range as calculated by formula (3), while it runs far beyond acceptable range as calculated by formula (4).

Equation (4) as originally obtained by van't Hoff[2] was limited to solutions so dilute that the heat involved in removing the necessary quantity of solvent was negligible. This heat of course is not the heat equivalent of the osmotic work, but the heat of dilution at constant concentration minus the heat equivalent of the osmotic work.

Let us now deduce equation (4) again, following van't Hoff in a general way but using solutions as concentrated as we choose, only requiring that the quantity of solution shall be so great that no appreciable change in concentration may be made when the necessary quantity of solvent is removed or added. That component whose vapor-pressure is measured shall be considered as the solvent.

[1] *Loc. cit.*

[2] *Ztschr. phys. Chem.*, I, 481 (*1887*).

We carry out an isothermal reversible cycle with the usual arrangement of a cylinder with frictionless piston, one end of the cylinder being closed by a diaphragm permeable to the solvent but not to the solute. Inside the cylinder is the large quantity of solution, outside the cylinder is the pure solvent. Temperature is equal to T. We press down on the piston. Thereby the solution is compressed until the pressure on it reaches the osmotic pressure π. Let β, be the coefficient of compression of the solution defined by

$$\beta = \frac{dv}{dp} \cdot \frac{1}{v}.$$

The work of this compression is

$$+\int_{p_2}^{\pi} V\beta_1 d\pi,$$

where V is the initial volume of the solution and p_2 is the vapor-pressure of the solvent over the solution.

We continue pressing, and the pure solvent now passes out. The work is kept up until so much of the solvent has passed out as contained one gram-molecule of solute; that is, N/n gram-molecules of solvent are pressed out. The work of this operation is

$$+\pi\varphi$$

where φ is the volume of the N/n gram-molecules of solvent.

After the solvent has passed through the diaphragm, it is released from the osmotic pressure and consequently expands, returning the work

$$-\int_{p_1}^{\pi} \varphi\beta_2 d\pi, \qquad (5)$$

where β_2 is the coefficient of compression of the pure solvent, and p_1 is the vapor-pressure over the pure solvent. It seems to me from what I have previously said[1] that we should in each case consider the coefficient of compression of the pure solvent only as entering into the operations, and not that of the solution at all. However, even if we do make a distinction in the two coefficients, the difference thereby introduced is vanishingly small, and we need not discuss this matter in any detail.

[1] This Journal, **22**, 579 (1898).

Heat energy, aside from the heat equivalent of the osmotic work, may be involved when the solution and solvent are separated, as already pointed out. Let Q be the heat involved when one gram-molecule of solvent is added to the solution under consideration. Then the heat involved in separating solution and solvent in the above operation is

$$\pm \frac{N}{n} Q.$$

The N/n gram-molecules of solvent are now vaporized isothermally at T. The work of this is

$$-p_1 v_1,$$

where v_1 is the volume of the vapor under p_1 pressure.

The vapor is now expanded isothermally to the volume v_2 corresponding to p_2 pressure. The work of this is

$$-\frac{N}{n} RTl \frac{p_1}{p_2}$$

where R is of course the gas constant.

The vapor is now brought into contact with the solution. But before this can be done, the pressure previously on the solution must be removed. In so doing the system returns nearly all the compression work, the slight deficiency in the return being due to the loss of the N/n gram-molecules of solvent, a deficiency which is very small even when at its maximum value but which in the present case is still smaller since a large part of the compression work belonging to the removed solvent has already been returned by the system, (5). The compression work now returned by the system is

$$-\int_{p_2}^{\pi} (V-\varphi)\beta_1 d\pi.$$

The solution is now ready to receive the vapor. The work of driving it in is

$$+p_2 v_2.$$

Now if heat is involved in separating solvent and solute osmotically in the first operation, then the same quantity of heat

but with opposite sign must be involved when the vapor is driven into the solution. So we have

$$\mp\frac{N}{n}Q.$$

Of course, this heat has nothing to do with the heat of condensation.

The isothermal reversible cycle is now complete and so,

$$+\int_{p_2}^{\pi} V\beta_1 d\pi + \pi\varphi - \int_{p_1}^{\pi} \varphi\beta_2 d\pi \pm \frac{N}{n}Q - p_1 v_1 - \frac{N}{n}RTl\frac{p_1}{p_2}$$

$$-\int_{p_2}^{\pi}(V-\varphi)\beta_1 d\pi + p_2 v_2 \mp \frac{N}{n}Q = 0,$$

and since for our purpose,

$$\int_{p_2}^{\pi} V\beta_1 d\pi = \int_{p_1}^{\pi} \varphi\beta_2 d\pi + \int_{p_2}^{\pi}(V-\varphi)\beta_1 d\pi,$$

we have

$$\pi\varphi = \frac{N}{n}RTl\frac{p_1}{p_2}$$

or

$$\frac{n}{N} = l\frac{p_1}{p_2}$$

as before.

It would appear then that the compressibility of the solution need not be considered, neither need the heat of solution be considered so far as this is independent of the osmotic work, a conclusion which is not in accord with that of others. Yet I cannot see what is wrong in my deduction, and I reach the same result when I follow Gouy and Chaperon,[1] for I cannot see how the vapor can be returned to the solution without releasing the pressure on it, nor how the solvent can be vaporized without releasing the pressure on it. Likewise the heat of separation seems to cancel with heat of mixing when the vapor is driven into the solution in the last operation.

In Arrhenius' method[2] of getting the osmotic pressure, the com-

[1] As given in Winkelmann's "Handb. d. Physik.," 1, 633.

[2] *Ztschr. phys. Chem.*, 3, 115 (*1889*).

pressibility of the solution likewise seems to disappear. The column of solution rises to a certain height h. The osmotic pressure is

$$\pi = hs_0$$

where s_0 is the density of the solvent.[1] When the column is so high that the hydrostatic pressure is considerable, the lower layers of liquid become more dense and hence a greater mass of liquid in the vertical column and apparently a greater osmotic pressure. But the pure solvent as it passes through the diaphragm is compressed itself and so its concentration is increased which balances the increased concentration of the solvent in the solution, using the word concentration in the sense of mass in unit volume. Similarly the concentration of the solvent in any particular layer of the solution is greater than the concentration of the solvent in any layer above that particular layer, and therefore will exert a pressure from the lower layer upwards, which upward pressure is proportional to the difference in concentration of the two layers and therefore to the density. The solute itself is of course equally distributed throughout the column of liquid. So it would seem to me that, although the mass in the column of solution is increased by the compression, yet the solvent as it enters becomes compressed, its concentration is increased, and therefore its osmotic activity is likewise increased, and we have as the measure of osmotic activity, only the concentration of the solute whatever the compression may be.

I do not see therefore where we can find any substantial correction for equation (2) so as to bring it into accord with observation. A correction may be brought in by considering that N refers to the molecular weight of solvent in the vapor state. In that state, the molecular weight is frequently somewhat greater than the simple chemical formula would give. Referring to formula (4) as applied to acetic acid as solute in benzene as solvent we see that an increase in M only makes matters worse, but that as applied to benzene as solute in acetic acid as solvent an increase in M would improve matters for solutions dilute in respect to benzene. Another correction may be brought in by considering that $RTl\frac{p}{p'}$ is only a true expression of work when

[1] This Journal, 22, 579 (1898).

the gases are true gases, and the vapors we are considering are by no means true gases. However, for all vapors which I could follow in tables, the corrections coming from this source were trifling.

I do not mean of course that equation (2) is wrong; I only mean that it does not give results in harmony with our ideas concerning the molecular weights of liquids in concentrated solutions, while equation (1) does give excellent results, and I cannot find sufficient reason why (2) should fail unless we look upon the osmotic laws as ideal laws to be kept out of actual experimental work.

We cannot at present therefore base equation (1) on equation (2), but must seek some other way of justifying it, a conclusion not reached in a previous paper.[1]

RUTGERS COLLEGE,
May 6, 1899.

HYDRASTINE HEXAIODIDE, AND THE ASSAY OF HYDRASTIS CANADENSIS BY MEANS OF STANDARD IODINE FOR HYDRASTINE AND OF STANDARD POTASSIUM IODIDE FOR BERBERINE.

BY H. M. GORDIN AND A. B. PRESCOTT.[2]

Received May 11, 1899.

WHEN a solution of iodine in potassium iodide is added to a solution of a salt of hydrastine a dense precipitate falls out, of a color varying from light brown to a very dark brown. In this order of mixing the alkaloidal solution with the iodine solution, different periodides seem to be formed in mixture, no matter whether the addition of iodine is stopped while the alkaloid is yet in excess or carried till the iodine is in excess. Even in the first case, that is, when the addition of iodine is stopped long before all the alkaloid is precipitated, the body formed only approaches a triiodide in composition, but does not correspond to a triiodide exactly. As will be seen from the accompanying analysis the total iodine of the periodide formed under these circumstances agrees quite well with the theoretical amount required by hydrastine triiodide, but the additive iodine is considerably below the amount required by that body. It

[1] *J. phys. Chem.*, **2**, 358 (*1898*).

[2] In the work of Research Committee D, Section II., Revision and Publication of the Pharmacopoeia of the United States.

will be noticed that there is a decided difference in this respect between hydrastine on one hand, and strychnine, brucine, and some other alkaloids on the other. The latter always form triiodides when iodine is added to an excess of a solution of their salt.[1]

But if the order of mixing be reversed, that is, the weak alkaloidal solution added to a large excess of iodine, a definite and unique periodide, namely, hydrastine hydriodide pentaiodide is always formed. This body is prepared according to the general method of making the higher alkaloidal periodides, described by us in the previous paper.[2] The hexaiodide thus made is a very dark brown powder, very difficultly soluble in ether, benzol, or cold chloroform, more readily in hot chloroform and in alcohol, and very easily in a mixture of alcohol and chloroform, or of alcohol and ether. In hot water it melts to a resinous mass. Attempts to crystallize it have failed, as on evaporation of the solvent it always remains a resinous mass.

Both in the hydrastine hexaiodide and the lower compound, that approaching a triiodide in composition, the so-called additive iodine was estimated by dissolving the substance in a small quantity of a mixture of alcohol and chloroform, and titrating with standard sodium thiosulphate. For the estimation of total iodine in these compounds, the substance was treated with zinc and ammonia, the iodine then liberated by means of a solution of nitrous acid in concentrated sulphuric acid, and taken up with carbon disulphide. The details were carried out exactly as described in our paper on morphine tetraiodide.[3]

ANALYSIS OF THE HYDRASTINE HEXAIODIDE.

For additive iodine: 0.1371 gram substance was found to contain 0.075833 gram additive iodine, and 0.1623 gram substance, 0.0898344 gram additive iodine.

Calculated for $C_{21}H_{21}NO_6HI.I_5$.	Found. I.	II.
55.43	55.30	55.34

For total iodine : 0.1491 gram substance contained 0.0996800 gram total iodine, and 0.1429 gram contained 0.0958333 gram total iodine.

1 This Journal, 20, 708 (*1898*).
2 *Loc. cit.*, 710 (*1898*).
3 This Journal, 20, 717 (*1898*).

Calculated for $C_{21}H_{21}NO_6HI.I_6$.	Found. I.	II.
66.52	66.86	66.06

ANALYSIS OF THE LOWER PERIODIDE OF HYDRASTINE, APPROACHING A TRIIODIDE.

For total iodine: 0.2674 gram contained 0.1337328 gram total iodine, and 0.2396 gram contained 0.1191752 gram total iodine.

Calculated for $C_{21}H_{21}NO_6HI.I_2$.	Found. I.	II.
49.83	50.01	49.74

For additive iodine: 0.09535 gram contained 0.0340975 gram free iodine, 0.1737 gram contained 0.0626681 gram free iodine, 0.1215 gram contained 0.04413953 gram, and 0.2328 gram contained 0.0838545 gram free iodine.

Calculated for $C_{21}H_{21}NO_6HI.I_2$.	Found. I.	II.	III.	IV.
33.22	35.76	36.07	36.33	36.02

In the iodometric estimation of hydrastine the exclusive formation of the hexaiodide is assured by adding a weak solution of the alkaloidal salt to a large excess of iodine. The estimation is carried out in the same way as described by us in a previous paper.[1]

The factor for hydrastine is 0.60403.

$$382.14 : 5 \times 126.53 :: 0.60403 : 1$$

In order to test this factor two solutions of hydrastine[2] in acidulated water were prepared, containing 0.3 per cent. and 0.15 per cent. of the free alkaloid, respectively, and the estimation of the strength of the solutions carried out exactly as described in the above-mentioned paper.

The results were as follows: Twenty cc. of the first (three-tenths per cent.) solution consumed 0.0970001 gram free iodine and twenty-five cc. of the second (0.15 per cent.) solution consumed 0.0611461 gram free iodine.

STRENGTH OF THE SOLUTIONS.

	Actually contained.	Found.
1	0.30	0.29
2	0.15	0.14

[1] This Journal, 20, 722 (*1898*).

[2] We are indebted to Prof. John Uri Lloyd, of Cincinnati, for a specially prepared sample of hydrastine. We had also a sample furnished us in a lot of pure alkaloids by Merck & Co. These two samples agreed very well with each other in the quantitative results.

PLAN OF THE ASSAY OF HYDRASTIS CANADENSIS.

The estimation of hydrastine and berberine in this root is based upon the following principles:

1. Hydrastine is quite soluble in absolute ether and forms, as we have just shown, a definite hexaiodide when a weak solution of any of its salts is added to a large excess of iodine dissolved in a potassium iodide solution.

2. Berberine on the contrary is completely insoluble in *absolute* ether.

This can be shown by rubbing up some pure berberine in a mortar with absolute ether, filtering, evaporating the ether and taking up with acidulated water. The liquid thus obtained is perfectly colorless and no trace of turbidity is produced in it, by Mayer's reagent, Wagner's reagent, or picric acid, nor does chlorine water produce the characteristic rose band.

3. Of all the difficultly soluble berberine salts the hydriodide seems to be the least soluble, particularly so in a very large excess of potassium iodide. If to a solution of berberine in water slightly acidulated with acetic or sulphuric acid, a large excess of a potassium iodide solution be added, the precipitation is so complete that the filtrate is almost entirely colorless, and no alkaloid can be detected in it by any of the above-mentioned reagents. Even chlorine water, reacting with a delicacy said to be one in 250,000, does not give any coloration, after removal of potassium iodide from the filtrate by silver nitrate, and of the excess of the latter by hydrochloric acid.

4. If to a very dilute solution of a salt of pure berberine about ten to fifteen times its amount of acetone be added and the solution then made strongly alkaline with solution of sodium hydroxide, berberine-acetone is so fully precipitated, particularly after ten or fifteen minutes' shaking, that the filtrate is almost completely colorless and no traces of alkaloid can be detected in it, after acidulation, by means of the above-mentioned reagents.[1] This berberine-acetone is easily decomposed by boiling with mineral acids, with the liberation of pure berberine.

These statements about berberine are true only when the berberine is perfectly pure, such as can be obtained from berberine-

[1] The compound of berberine with acetone was first made by Gaze: *Arch. d. Pharm.*, (*1890*), 607.

acetone according to the directions of Gaze[1] and dried in the air without heat. Commercial salts of berberine and particularly commercial berberine itself is generally so impure that some of these reactions will not hold good.[2]

Basing ourselves upon these facts we have worked out a

[1] *Loc. cit.*

[2] Beside berberine and hydrastine one other alkaloid has been found in Hydrastis, but in proportions quite too small to have any bearing upon the assay percentages, either of berberine or hydrastine. That the assay process here proposed leaves no appreciable quantity of any alkaloid behind we have verified by operating upon a considerable quantity of the drug. After removing the hydrastine with the ether and the berberine with potassium iodide, there was nothing left that gave indications of alkaloidal character. What has been learned of canadine makes it probable that it would adhere to berberine or to hydrastine. In the elaborate research which has established the existence of canadine, Prof. E. Schmidt (*Arch. d. Pharm.*, **232**, 136 (*1894*)) prepared it from a crude hydrastine, and also from a crude canadine hydrochloride made for him by E. Merck, of Darmstadt. In the purification the canadine was precipitated as a salt of nitric acid. The insolubility of its salts with mineral acids would be likely to carry it into the crude salts of berberine, when these are precipitated for the removal of this alkaloid. Prof. J. U. Lloyd ("Drugs and Medicines of North America," Cincinnati, pp. 139-141, 127 (*1885*)), has shown that strong acidulation with hydrochloric acid is necessary to the full precipitation of the berberine, and that when the filtrate is precipitated by ammonia at the neutral point, any further precipitation caused by an excess of ammonia consists of or contains berberine, as a result of its incomplete removal by acid precipitation. Prof. Lloyd was evidently right in his conclusion that the method of Burt (*Am. J. Pharm.*, **47**, 481 (*1875*), for "a third alkaloid" yields berberine unless this has been more closely removed by the strong acidulation just referred to. But since the research of Schmidt it appears likely that canadine would be precipitated with the berberine by strong acidulation. And the discrepant accounts of the color of the third alkaloid are explained by the discovery that though it is colorless, in purity, it acquires color by exposure to light and air, tetrahydroberberine ($C_{20}H_{21}NO_4$) being oxidized into berberine itself ($C_{20}H_{17}NO_4$) (Schmidt: *Arch. d. Pharm.*, **232**, 148 (*1894*)). However, neither Hale nor Burt worked with enough of the Hydrastis to obtain canadine in the purity and amount required for any satisfactory description or conclusion. They did not claim to individualize or name the alkaloid; indeed the note of Hale only raised the question of its existence. Prof. Schmidt, who had, as he said, worked more than ten years with Hydrastis alkaloids, found it needful to operate upon fifty kilograms of the drug, and availed himself of a crude product accumulated in a manufactory. This was about five years after Wilhelm had made a report from the laboratory of Prof. Schmidt (*Arch. d. Pharm.*, **226**, 330 (*1888*)), upon a third alkaloid in Hydrastis. In this report the finding of this alkaloid was ascribed to Hale (*Am. J. Pharm.*, **45**, 247 (*1873*)), Burt (*loc. cit.*), and Lerchen (*Am. J. Pharm.*, **50**, 470 (*1878*)), and the reader might infer that the name, canadine, had been proposed by Hale and Burt. Consequently in the second edition of "Beilstein" (III, 491) "canadine" is described upon no other authority than that of Hale and of Burt. In Beilstein's third edition, with fuller description, the authority of E. Schmidt, Privatmitth., is prefixed. The alkaloid examined by Wilhelm in 1888, not analyzed because of insufficient quantity, was prepared from ammoniacal solution by extraction with acetic ether. That observed by Hale, by Burt, and by Lerchen was obtained by precipitation with ammonia in some excess. The first elementary analysis was made by L. Deichmann (Inaugural dissertation, Rostock, 1892). In the analysis of Schmidt his figures differ from those of Deichmann, from greater purity of preparation (*Arch. d. Pharm.*, **232**, 139 (*1894*)). Deichmann reported a cryoscopic determination of the molecular weight. Zeisel (Inaugural dissertation, Dorpat, 1892) determined the methoxy groups in canadine.—A. B. PRESCOTT.

method of assaying Hydrastis Canadensis, the plan being as follows: The alkaloids of the powdered root are first set free by the action of an ether-ammonia mixture, consisting of stronger ammonia water five cc., alcohol five cc., and ether thirty cc.[1] After drying, the powder is extracted with absolute ether and the ethereal extract, after evaporation of the ether and taking up the residue with acidulated water, is used for the estimation of hydrastine by any suitable method. Through the powdered root left in the extraction apparatus air is passed till it is dry, and then the powder is extracted with alcohol to exhaustion. The alcoholic extract, after dilution with water, evaporation of the alcohol and taking up the residue with diluted acetic acid, is used for the estimation of berberine. The berberine is first precipitated as berberine-acetone, the latter washed, decomposed by the aid of acid, and the purified berberine estimated by standard solutions of potassium iodide, silver nitrate, and ammonium thiocyanate.

DIRECTIONS FOR THE ASSAY.

Ten grams of the finely powdered Hydrastis are rubbed up to a paste with a few cc. of the above-mentioned ether-ammonia mixture in an eight ounce, screw-top ointment jar, and a few cc. more of the same mixture are then added so as to have the powder well covered with liquid. The small pestle is then left inside, and the jar well covered is set aside over night. The jar is then opened, put into a good current of air till the odor of ammonia has disappeared, and then in a vacuum over sulphuric acid for about five or six hours. The powder is then put into a filter-paper cell, placed in a Soxhlet extraction apparatus, the jar rinsed out several times with powdered glass or in the absence of this with coarsely powdered barium nitrate, the rinsings added to the Soxhlet, the latter connected with an Erlenmeyer flask containing about forty or fifty cc. absolute ether, and the extraction conducted in the usual way, till a few drops after evaporation of the ether and acidulation give no reaction with Mayer's or Wagner's reagent. The ethereal extract will be found to

[1] This is the same mixture we have used in our general method of extracting alkaloids (This Journal, 21, 232 (*1899*)), with the omission of chloroform. The latter gives with berberine a compound not decomposable by acids (E. Schmidt. *Pharm. Ztg.*, (*1887*), 542).

have only a very slight yellow color. The Erlenmeyer is then detached from the Soxhlet, the ether poured out into a flat evaporating dish, the Erlenmeyer washed out several times with water containing about two per cent. sulphuric acid, the washings added to the contents of the evaporating dish, and the latter put into a draught at about 30° C. till the ether has disappeared.

The contents of the dish are poured into a 100 cc. flask, the dish washed, the washings added into the flask and the latter filled up to the 100 cc. mark. The solution containing hydrastine sulphate, and of which every ten cc. represent one gram of the root, is used for the estimation of hydrastine.

For the iodometric estimation twenty cc. of the filtered solution (representing two grams of the drug) are run from a burette into a 100 cc. flask containing twenty or thirty cc. of a standardized solution of iodine of any known strength (that in the neighborhood of one per cent. is the best) and the analysis carried out exactly as described in our previous paper.[1] From the amount of iodine consumed the amount of hydrastine is deduced by using the factor of the hydrastine hexaiodide, *i. e.*, 0.60403 gram of hydrastine for one of iodine consumed.

For a gravimetric estimation another portion of twenty cc. of the filtered solution is run into a separator and the hydrastine shaken out with benzene and ammonia. All the coloring-matter remains in the aqueous liquid, and a perfectly colorless solution of hydrastine in benzene is obtained. The benzene solution is then filtered through a small filter into another separator, the first separator and filter washed with benzene and the hydrastine again shaken out with water acidulated with sulphuric acid. At last from the watery solution the hydrastine is shaken out with ether and ammonia, the ether poured into a tared beaker and slowly evaporated in a dark place. After drying in a vacuum over sulphuric acid and paraffin the beaker is weighed. The hydrastine is left in perfectly white crystals, and only a slightly yellowish tint can be seen on the sides of the beaker. This tint is probably due to traces of canadine, which becomes yellow[2] on exposure to the light. Of course instead of shaking out, the method of perforation may be used if preferred.

[1] This Journal, 20, 722 (*1898*).

[2] E. Schmidt: *Arch. d. Pharm.*, 232, 141 (*1894*).

For the estimation of berberine a current of dry air is passed through the Soxhlet till all the ether is removed, the Soxhlet connected with an Erlenmeyer containing forty or fifty cc. of alcohol, and the extraction continued until the alcohol comes out colorless. The alcoholic extract containing the berberine, and considerable quantities of extractive matter, is poured out into an evaporating dish, the Erlenmeyer washed out with hot water and a little dilute acetic acid, the washings added to the evaporating dish and the latter kept on a water-bath, adding water from time to time till all the alcohol has disappeared. A little more diluted acetic acid is now added, the dish covered and when completely cold its contents are filtered into an Erlenmeyer having the capacity of about three or four hundred cc.[1]

Six to eight cc. of acetone are added to the contents of the Erlenmeyer, to which the washings of the dish and the filter have been added, and then a ten per cent. solution of sodium hydroxide is added, drop by drop, till the precipitate first formed ceases to disappear on shaking, and the liquid acquires a strongly alkaline reaction. The Erlenmeyer is then stoppered and shaken in a circular direction for about ten or fifteen minutes, and then set aside in a cool place for two or three hours. The berberine-acetone separates out in crystals, some of which adhere to the sides of the vessel. The supernatant liquid is then poured on a small filter, the precipitate washed once or twice by decantation and then on the filter till the washings are colorless. The filter is then pierced and, by means of the wash-bottle, the precipitate is returned to the same Erlenmeyer in which the precipitation took place. In this way all loss is avoided. To the precipitate about four or five cc. of a five per cent. solution of sulphuric acid is now added and then water enough to make about one or two hundred cc. The Erlenmeyer is now put into hot water when the precipitate will completely dissolve in the course of a few minutes. The solution is now poured out into a long-necked flask, washing the Erlenmeyer several times, the

[1] In the remaining procedure, the simplest way would be to precipitate the berberine with hydrochloric or nitric acid, but in this case a considerable amount of extractive matter contaminates the precipitate and too high a yield would result though the error in this respect might be compensated to some extent by the solubility of the hydrochloride or nitrate in water. But the *best* way is to purify the berberine by converting it into berberine-acetone, regenerate the alkaloid by means of sulphuric acid and then estimate it volumetrically by standard potassium iodide.

flask put on an asbestos plate and kept very gently boiling for about an hour and a half or two hours, adding hot water from time to time if necessary.

The flask is now cooled and its contents poured out into a liter measuring flask[1] into which there has been previously taken from a burette one hundred cc. of twentieth normal potassium iodide. The flask is washed several times, the washings added to the measuring flask and the latter filled up to one liter and set aside over night. Five hundred cc. are now filtered off into another liter flask, fifty cc. of twentieth normal silver nitrate, and nitric acid, added to the flask, which is filled up to one liter, well shaken, filtered, and five hundred cc. of the filtered liquid titrated back with fortieth-normal ammonium thiocyanate, using ferric alum as indicator. Twice the number of cubic centimeters of the thiocyanate solution used is equal to the number of cubic centimeters of the potassium iodide solution consumed by the berberine, representing ten grams of the Hydrastis root. By multiplying the number of cubic centimeters of twentieth normal potassium iodide consumed, by 0.167125, the percentage of anhydrous berberine in the root is obtained, as one cc. of the potassium iodide solution is equal to 0.0167125 gram of berberine.

In our assay of Hydrastis Canadensis three samples of powdered Hydrastis were treated in the way described. The berberine was estimated volumetrically, the hydrastine both iodometrically and gravimetrically.

FOR HYDRASTINE.

	Iodine consumed by two grams of the root.	Hydrastine. Iodometric.	Gravimetric.
1	0.0760015	2.29	2.29
2	0.0772012	2.33	2.30
3	0.0777770	2.35	2.28

FOR BERBERINE.

	Number of cc. of twentieth normal KI consumed by ten grams of the root.	Berberine, anhydrous.
1	15.1	2.52
2	15.3	2.55
3	14.8	2.47

With regard to the precipitation of berberine by potassium

[1] The berberine hydriodide being extremely bulky the error arising from the space occupied by the precipitate is reduced to a minimum by using a large flask.

iodide we wish to draw attention to the fact that even a solution of the free alkaloid without any addition of acid is precipitated by potassium iodide. As there is no acid to combine with the potassium the question is, what becomes of the metal when the iodine of the potassium iodide is taken up by the berberine? That there is no potassium in the precipitated berberine hydriodide was proved by igniting the precipitate with sulphuric acid and ammonium nitrate, when no trace of residue was to be found. All the potassium must then pass into the filtrate and part of it must exist there as a salt of something acting as an acid, as there is no trace of alkalinity in the filtrate. No one of the indicators gives an alkaline reaction. We acidulated the filtrate with sulphuric acid, shook it up with ether, washed the ether till there was no reaction given for iodine by sodium nitrite and starch, nor for sulphates by barium chloride, and evaporated the ether to dryness; a very small amount of a crystalline substance was left, which would seem to indicate the presence of an organic acid, but the quantity was too small for a closer examination. We intend to take a larger quantity of pure berberine into operation and investigate the subject thoroughly in the near future.

UNIVERSITY OF MICHIGAN,
April, 1899.

UPON THE ACTION OF DIAZO COMPOUNDS ON THYMOLPARASULPHO ACID.

[SECOND PAPER.]

BY JAMES H. STEBBINS, JR.

Received May 16, 1899.

IN my former paper[1] I described several azo compounds obtained by combining diazobenzene chloride, diazoparatoluene chloride, and diazoxylene chloride with thymolparasulpho acid.

Contrary to precedent, it was observed that the three compounds named, notwithstanding their increasing molecular weight, were all possessed of about the same yellow color, and were all three more or less unstable, being partially decomposed by boiling water.

It therefore seemed of interest to ascertain in what manner the

[1] This Journal, 3, 112.

sulpho acids of higher diazotized amines would behave towards thymolparasulpho acid. With this end in view, the following experiment was made:

ACTION OF NAPHTHIONIC ACID ON THYMOLPARASULPHO ACID.

One twenty-eighth mol. of eighty-three per cent. sodium naphthionate, or 10.4 grams, were dissolved in 200 cc. of water, and to it were added one twenty-eighth of two mols. of hydrochloric acid of 1.20 sp. gr., or six and four-tenths grams. Furthermore one twenty-eighth mol. of seventy-nine per cent. sodium sulphite ($NaNO_2$) or two and nine-tenths grams were dissolved in fifty cc. of water, and the solution thus obtained was gradually stirred into the naphthionate solution.

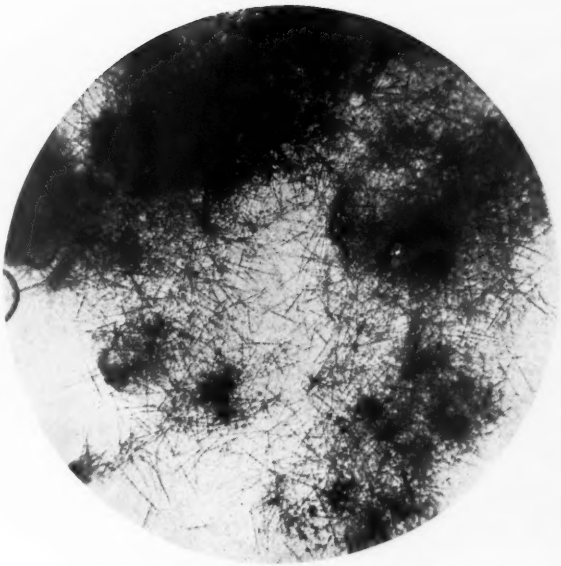
The diazonaphthionic acid thus formed, was then slowly run, under constant stirring, into a cooled solution of one-twenty-eighth mol. thymolparasulpho acid, or eight and two-tenths grams, dissolved in 100 cc. of water made alkaline with four and three-tenths grams of caustic soda.

The mixture at first turns bright red, but gradually increases in depth of color, as the diazo solution is run in, till at last the solution assumes a deep red-brown color, tinged with a suspicion of crimson, which latter color becomes all the more manifest if a drop of the solution be placed upon filter-paper. This phenomenon would suggest a mixture of two colors; *viz.*, a brown and a crimson color.

Some foam is formed during the operation, but whether this is due to an evolution of nitrogen, or to the presence of carbonates in the caustic soda used, I am at present unable to say. The reaction mixture was allowed to stand over night and was then heated to boiling, and saturated with dry sodium chloride.

A reddish brown precipitate A is thus thrown down, and was collected upon a filter and dried.

The filtrate B contains a crimson-red dye-stuff which is so exceedingly soluble in water that it was found next to impossible to precipitate it with salt. A small quantity, however, was obtained by saturating the filtrate at a boil with a large excess of salt, and filtering from the brownish red precipitate formed. Even after this treatment a considerable quantity of the coloring-matter remains in solution. It may, however, be precipitated



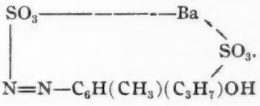
Ba-Salt Naphthionic Acid Azothymolparasulpho Acid.

with barium chloride as a barium salt, but the yield was so small that an examination of the product had to be abandoned for the present.

Brown Precipitate A.—The brown product precipitated with salt, and alluded to above, was dissolved in water, filtered, and treated with an excess of barium chloride. A copious yellow-brown precipitate C of a barium salt was thrown down. This was collected upon a filter, and washed with cold water until free from all excess of barium chloride, and then dried. The filtrate from this barium salt contains a purplish red dye-stuff in solution, which seems to be identical in color with the dye-stuff contained in filtrate B. From this it would therefore seem, that two coloring-matters are formed by the action of diazonaphthionic acid on thymolparasulpho acid, one of which is brownish, and easily precipitable by sodium chloride or barium chloride, and the other purplish red to crimson, and so very soluble in water that it is only precipitated therefrom with great difficulty by either sodium chloride or barium chloride. The latter is, however, only formed in very small quantity, and its great solubility in water would indicate that it contains more than two sulpho groups. It is therefore possible that it owes its formation to the presence of a small quantity of thymoldisulpho acid, in the thymolparasulpho used.

The barium salt C, in a moist condition, is fairly soluble in boiling water, but once dried its solubility is greatly diminished. It is slightly soluble in boiling ninety-five per cent. alcohol, but readily soluble in proof spirit. It may be obtained in a crystalline form, by dissolving it in boiling water, and allowing it to cool slowly. It is thus obtained as a perfect network of orange-colored hair-fine needles. (See plate.)

BARIUM ESTIMATION.

	Gram.
Substance taken	0.5379
Barium sulphate found	0.1939
	Per cent.
Equivalent to barium	24.43
Theory for $C_{10}H_6$ 	22.87

It is therefore probable that the compound under examination is represented by the above formula.

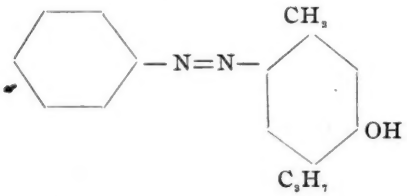
G. Mazzara and G. Posseto[1] on treating thymol in alkaline solution with diazobenzene chloride obtained a mixture of monophenylazothymol, $C_6H_5—N_2—C_6H_2(CH_3)(C_3H_7)—OH$ and monophenyldisazothymol $(C_6H_5N_2)_2C_6H(CH_3)(C_3H_7)(OH)$.

The former of these two products on reduction with tin and hydrochloric acid, and then oxidation of the reduction product with ferric chloride, gave a thymoquinone melting at 45°, while the diazo product by the same treatment, gave an oxythymoquinone melting at 167°–169°.

From this they conclude that the phenylazothymol obtained has the following constitution:

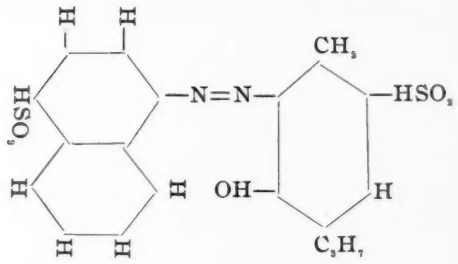
$$C_6H_2(\overset{\text{I.}}{CH_3})(\overset{\text{IV.}}{C_3H_7})(\overset{\text{III.}}{OH})(\overset{\text{VI.}}{C_6H_5N_2}).$$

The above expressed graphically would give us the following:

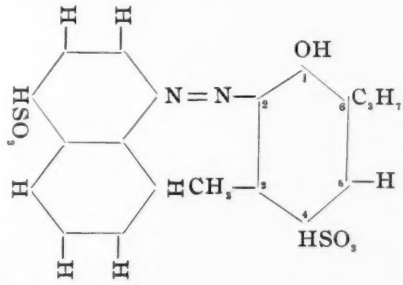


If we now consider the naphthionic acid azothymolparasulpho acid, $C_{10}H_6N_2C_6H(CH_3)(C_3H_7)(OH)HSO_3$, above alluded to, and produced by the action of diazonaphthionic acid, on thymolparasulpho acid, it will be seen that as the sulpho group in the thymol ring, occupies the para position with relation to the OH group, there are only two other positions for the diazo group to enter; *viz.*, the ortho and the meta positions, but from the general rules governing the formation of azo compounds, it is evident that the diazo group must enter the ortho position with relation to the OH group, and hence the constitution of this compound may probably be represented as follows:

[1] *Gazz. chim. ital.*, **15**, 52.



Or using a somewhat less antiquated formula for thymolparasulpho acid, we would get



It will therefore be seen from the foregoing, that the union of thymolparasulpho acid with diazo compounds of the naphthalene series, produces brownish, to crimson coloring-matters, in contradistinction to those obtained with the diazo compounds of the benzene series.

A parallel test made with diazobetanaphthalenesulpho acid (Casella's acid), and sodium thymolparasulphonate has shown that here too a reddish brown coloring-matter is formed.

It was intended at the beginning of this investigation, to go into the matter more at length, but circumstances which I had not foreseen have forced me to suspend my work, and to present it in its present unfinished condition.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

A NEW VOLUMETRIC METHOD FOR MAGNESIUM.[1]

BY RICHARD K. MEADE.

Received June 5, 1899.

ONE of the elements for which, so far, no satisfactory volumetric method of determination, of general application, has been found, is magnesium. Stolba[2] suggested a volumetric method depending upon the fact that one molecule of magnesium ammonium phosphate required two molecules of mineral acid for solution. Hart and Sutton both describe the method in detail, in their works upon volumetric analysis, and call attention to its accuracy. Hartzell, a student in the laboratory of Lafayette College, in his thesis work for graduation, in 1897, made use of the method in determining magnesia in cement and the result of his investigations, also, showed the method to be fairly accurate. The great objection to Stolba's method, particularly if it is resorted to as a time-saver, is the tedious washing of the precipitated magnesia with alcohol, in order to get rid of the ammonia, making the volumetric determination very little if any quicker than the gravimetric. In any event, so far as I know, the method is very little if ever used even in commercial laboratories where magnesia determinations are a part of the daily routine.

Analogous to the phosphates are the arsenates. If instead of adding sodium phosphate to an ammoniacal solution containing magnesium we add sodium arsenate, magnesium ammonium arsenate, corresponding to magnesium ammonium phosphate, is precipitated. This reaction is of course a familiar one, since it is the one upon which the usual gravimetric determination of arsenic is based. Now if the magnesium in a solution can be entirely precipitated as a double arsenate of magnesium and ammonium, if the magnesium and arsenic in this compound bear a fixed ratio to each other, if the precipitate can be collected and washed free from sodium arsenate, then clearly any volumetric method which will give us the weight of arsenic in the precipitate

[1] Read before the Lehigh Valley Section of the American Chemical Society, May 16, 1899.

[2] *Chem. Centrbl.* (*1866*), 728.

will also tell us indirectly the amount of magnesium in the solution. From the formula of the double salt, $Mg_2(NH_4)_2As_2O_8 + H_2O$, it will be seen that one atom of magnesium is equivalent to one atom of arsenic and consequently the ratio between the magnesium and arsenic is 24.28 : 75.01.

As the first step looking to the formulation of a volumetric method along these lines, a stock solution of magnesium was prepared as follows: Fifty grams of pure magnesium chloride were dissolved in about 700 cc. of water and a little ammonium oxalate added to precipitate any traces of calcium present. The solution was allowed to stand for a day when the very slight precipitate of calcium oxalate was filtered off. A sufficient quantity of ammonium oxalate to convert all the magnesium in the solution to magnesium oxalate was next added and the solution evaporated to small bulk over a water-bath. The separated magnesium oxalate was collected, washed, dried, and ignited, first at a low temperature and then at a higher until finally at a red heat. Of the pure magnesium thus obtained, five grams were dissolved in dilute hydrochloric acid and the solution diluted to two liters. Each fifty cc. of this solution should have been equivalent to 0.2500 gram of magnesium oxide. Checked by precipitation with sodium phosphate, fifty cc. gave:

I. 0.6900 gram of $Mg_2P_2O_7$ equivalent to 0.2497 gram of MgO.
II. 0.6891 gram of $Mg_2P_2O_7$ equivalent to 0.2493 gram of MgO.

Checked by evaporation to dryness and ignition of the residue, fifty cc. gave:

0.2490 gram of MgO.
0.2498 gram of MgO.

The average of the four determinations is 0.2495 gram MgO.

A search into the literature on the solubility of the magnesium ammonium arsenate showed the precipitate to be less soluble where an excess of sodium arsenate was present in the ammoniacal solution; accordingly, wherever the magnesium was precipitated by sodium arsenate, a considerable excess of the precipitant was used. The precipitate of course must be washed with dilute ammonia water and, as it is not entirely insoluble in this medium, the volume of the washing fluid should be kept as small as possible.

Following these points, fifty cc. of the stock solution were diluted to 500 cc. and 50 cc. of sodium arsenate (ten per cent.) solution added; then ammonia, drop by drop, with constant stirring until the precipitate began to form. At this point the addition of ammonia was interrupted and the solution stirred for five minutes after which one sixth the volume of the solution of strong ammonia was added and the mixture stirred for five minutes longer and allowed to stand over night. In the morning the precipitated magnesium ammonium arsenate was collected in a Gooch crucible, dried, and ignited at a very low temperature and weighed as magnesium pyroarsenate, containing 25.94 per cent. of magnesium oxide. The results were:

No.	$Mg_2As_2O_7$ Gram.	Equivalent to MgO. Gram.
1	0.9599	0.2490
2	0.9545	0.2476
3	0.9592	0.2488
4	0.9573	0.2483
Average		0.2484
Instead of		0.2495
Difference		0.0009

As a further test the magnesia from fifty cc. of the stock solution was precipitated as described, dissolved in dilute hydrochloric acid and the arsenic thrown out of solution with hydrogen sulphide. The magnesium remaining, was then determined as pyrophosphate with the following results:

No.	$Mg_2P_2O_7$. Gram.	Equivalent to MgO. Gram.
1	0.6883	0.2490
2	0.6865	0.2484
3	0.6870	0.2486
Average		0.2487
Instead of		0.2495
Difference		0.0008

In the same manner, the magnesium in fifty cc. of the stock solution was precipitated as magnesium ammonium arsenate, dissolved in hydrochloric acid and the arsenic determined as magnesium pyroarsenate by addition of magnesia mixture. The results were:

No.	$Mg_2As_2O_7$. Gram.	Equivalent to MgO. Gram.
1	0.9590	0.2488
2	0.9536	0.2474
3	0.9552	0.2478
Average		0.2481
Instead of		0.2495
Difference		0.0014

These three sets of results while a little low, showing that a slight loss of magnesia is incurred, probably due to solution of the precipitate in the mother-liquor and the wash-water, nevertheless, fall well within the limits of allowable variation for technical work, and show the ratio between the magnesium and arsenic to be constant.

The next step was to find a suitable volumetric method for determining the arsenic. This being in the state of arsenic acid excluded all methods supposing the element to be in the condition of lower oxidation. The methods of Pierce and McCay depending upon the precipitation of the arsenic as silver arsenate by an excess of standard silver nitrate and the determination of, either the silver in the precipitate or the excess of silver in the solution, by titration with sodium thiocyanate were also not considered, as both time and expense made them unsuitable for commercial work.

Of the methods depending upon the reduction of the arsenic to arsenious acid and the titration of the latter by standard iodine, that making use of the reaction between arsenic acid and potassium iodide in acid solutions offered the best field for investigation and following the method as laid down by Gooch and Browning,[1] several determinations were made. The process followed consisted in dissolving the precipitated arsenate in dilute sulphuric acid, adding an excess of potassium iodide and ten cc. of sulphuric acid (1 : 1) and diluting to 100 cc. The solution was boiled rapidly until the volume reached 40 cc. and the free iodine in the solution destroyed by careful addition of sulphurous acid (roughly made about one-half normal). Sodium carbonate was then added until the solution was nearly neutral and next an excess of sodium bicarbonate over what was required to make it so. The arsenious acid was then titrated with standard iodine

[1] *Am. J. Sci.* (3), 40, 66.

solution. This latter was made by dissolving 52.24 grams of pure resublimed iodine in a solution of 75 grams of potassium iodide in 200 cc. of water and diluting to one liter. Each cubic centimeter of this solution should be equivalent to 0.005 gram of magnesium oxide. The following satisfactory results were obtained by this method.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	Iodine required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.6	0.2480
2	50	0.2495	49.7	0.2485
3	25	0.1247	24.9	0.1245
4	25	0.1247	24.9	0.1245
5	10	0.0499	9.9	0.0495
6	10	0.0499	10.0	0.0500

The time required to determine the arsenic by this method was from one-half to three-quarters of an hour.

The next, and the method finally adopted as the one most suited to the volumetric determination of magnesium, was the one worked out by A. Williamson and described by him in the *Journal of the Society of Dyers and Colourists*, May, 1896. A description of the method is also to be found in Sutton's "Volumetric Analysis," page 369.

It depends like the method of Gooch and Browning upon the reaction between arsenic acid and potassium iodide. Williamson found that where a solution of arsenic acid contained sufficient sulphuric or hydrochloric acid the arsenic is quickly reduced from the higher to the lower state of oxidation, even in the cold, according to the reaction

$$As_2O_5 + 4KI + 4HCl = As_2O_3 + 4KCl + 2H_2O + 2I_2.$$

For every molecule of arsenic acid reduced, corresponding to two atoms of magnesium, two molecules or four atoms of iodine are liberated. This latter is titrated with sodium thiosulphate and from the amount of standard solution required the magnesium calculated.

The process followed consisted in dissolving the precipitated magnesium ammonium arsenate in dilute hydrochloric acid, washing the filter-paper well with the acid and, after adding potassium iodide and allowing to stand for a few minutes, titrating with standard thiosulphate. This latter corresponded, cubic

centimeter for cubic centimeter, with the iodine solution mentioned above. Below are the results.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	"Hypo" required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.8	0.2490
2	50	0.2495	49.9	0.2495
3	25	0.1247	25.0	0.1250
4	25	0.1247	24.9	0.1245
5	10	0.0499	9.95	0.0498
6	5	0.0249	5.0	0.0250

Determinations required only from seven to ten minutes by this method after the arsenic was in solution and were just as accurate as those by the longer method of digestion with potassium iodide.

The attempt was next made with success to hasten the precipitation of the magnesium by violent agitation. Fifty cc. of the stock solution were measured into a large Erlenmeyer flask, diluted to about 500 cc. and one-third this volume of strong ammonia and 50 cc. of a ten per cent. solution of sodium arsenate added, the flask corked up tightly and shaken violently by hand for ten minutes. After allowing the precipitate to settle, it was filtered and the arsenic determined as described above.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	"Hypo" required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.9	0.2495
2	50	0.2495	49.9	0.2495
3	25	0.1247	24.8	0.1240
4	15	0.0748	15.0	0.0750
5	10	0.0499	9.9	0.4950
6	5	0.0249	4.9	0.0245

The time required for the precipitation, filtration, washing, re-solution, and titration, had now been shortened to about three-quarters of an hour.

The standard thiosulphate was titrated against standard sodium arsenate, prepared by dissolving 12.29 grams of pure arsenious acid in nitric acid, evaporating to dryness on a water-bath, neutralizing with sodium carbonate and diluting to one liter. Each cc. of this solution was equivalent to 0.005 gram of magnesium oxide. The values obtained by titration of the standard thiosulphate against this solution coincided with those

obtained by titration with standard iodine solution. The values obtained by titration against standard bichromate and potassium iodide did not differ materially from those obtained by titration against standard arsenate or standard iodine.

The method finally worked out is as follows:

Pour the solution, which should not contain too great an excess of ammonium chloride or ammonium oxalate, into a large Erlenmeyer flask or a gas-bottle of sufficient capacity. Add one third the volume of the solution of strong ammonia and fifty cc. of sodium arsenate. Cork up tightly and shake vigorously for ten minutes. Allow the precipitate to settle somewhat, and wash with a mixture of three parts water and one part strong ammonia, until the washings cease to react for arsenic. Avoid using an excess of the wasning fluid, however. Dissolve the precipitate in dilute hydrochloric acid (1 : 1), allowing the acid solution to run into the flask in which the precipitation was made, and wash the filter-paper with the dilute acid, until the washings and solution measure 75 or 100 cc. Cool, if not already so and add from three to five grams of potassium iodide, free from iodate; allow the solution to stand a few minutes and then run in the standard thiosulphate until the color of the liberated iodine fades to a pale straw color. Add starch and titrate until the blue color of the iodide of starch is discharged. If preferred, an excess of thiosulphate may be added, then starch and standard iodine until the blue color is produced. On adding the iodide of potassium to the acid solution, a brown precipitate forms which, however, dissolves when the thiosulphate is added.

Below are some results upon the method as given above:

Sample.	MgO. Gravimetric. Per cent.	Thiosulphate required. cc.	MgO. Volumetric. Per cent.
Dolomite	21.78	43.3	21.65
		43.4	21.70
Limestone	9.16	18.2	9.10
		18.2	9.10
Slag	16.42	32.6	16.30
		32.5	16.25
Cement, Portland	2.57	5.1	2.55
Cement, Natural	11.03	22.0	11.00
		22.2	11.10

EASTON, PA.,
May 15, 1899.

NOTES ON ALKALI SOIL IN MONTANA.

By F. W. Traphagen and W. M. Cobleigh.

Received April 24, 1899.

EVEN the most casual observer, passing through the state by rail, must have been more or less impressed by the appearance of occasional spots, barren of vegetation, and incrusted with a white, red or yellow salt, which are to be seen at various points in Montana. These are the so-called "alkali" soils, and represent the worst phase of the condition.

The agriculturist recognizes two kinds of alkali: the "white" and the "black," the former consisting mainly of sodium sulphate and the latter of sodium carbonate.

A solution of the "black" alkali, on account of its solvent action upon organic matter, dissolves the humus from the soil, and upon evaporation leaves it as a shiny black coating upon the surface, or in black concentric rings around the pools in which it collects. Vegetation is destroyed by contact with solutions of sodium carbonate, the stems, especially at the surface of the ground, being frequently completely girdled. Hilgard has found that as little as one-tenth per cent. sodium carbonate in the surface foot is deleterious.

On the other hand a much larger amount of the "white" alkali may exist without affecting vegetation injuriously. In Montana, the alkali consists almost entirely of sulphates and rarely possesses a strong alkaline reaction. I have found crops thriving in the presence of as much as six-tenths per cent. of the "white" alkali. The "white" alkali seems to produce its injurious effects when present in excess, not through any chemical influence, but rather by interference with the process of osmosis by which the plant obtains its mineral food and water, the external solutions frequently becoming of much greater density than the sap.

The following analyses of typical alkali soils of the Yellowstone Valley, will give an idea of the salts usually present and their relative proportions.

Sample No. 372, from Hesper Farm, uncultivated portion, taken at fourteenth foot in depth, about the center of "zone of

concentration." The figures give actual percentage of constituents soluble in water.

SAMPLE NO. 372, HESPER FARM.

	Per cent.
Soluble silica	0.004
Calcium sulphate	0.150
Magnesium sulphate	0.130
Potassium sulphate	0.009
Sodium sulphate	0.320
Sodium nitrate	0.018
Alkalinity in terms of sodium carbonate	0.096

SAMPLE NO. 304, SURFACE CRUST.

	Per cent.
Soluble silica	0.054
Calcium sulphate	1.28
Magesium sulphate	14.91
Potassium sulphate	0.83
Sodium sulphate	26.65
Sodium nitrate	trace
Sodium chloride	0.637
Alkalinity in terms of sodium carbonate	0.144

SAMPLE NO. 405, SURFACE CRUST.

	Per cent.
Soluble silica	0.035
Calcium sulphate	1.38
Magnesium sulphate	3.21
Potassium sulphate	0.18
Sodium sulphate	6.43
Sodium nitrate	0.091
Sodium chloride	0.578
Alkalinity in terms of sodium carbonate	0.048

It will be seen that the actual percentage of soluble matter present varies very greatly, but the ratios of the quantities of the different salts is remarkably constant.

All regions of deficient rain-fall are subject to the accumulation of soluble salts in their soils, for, unlike humid sections, there is an insufficient quantity of water to carry off the salts rendered soluble by the natural processes of rock-disintegration.

Add to this the presence of rocks of marine origin which have been deposited in the presence of sulphates and chlorides, and you have a fruitful source of soluble alkali salts.

Analyses of the Fort Benton shales, bordering the Yellowstone

Valley, show the presence of considerable quantities of soluble sulphates. The percentages calculated to sodium sulphate range from 1.03 to 2.02. As these rocks, by their decomposition, contributed very largely to the formation of the soils of the Valley, the source of the "alkali" is readily apparent.

Where the soil exists in its virgin condition, undisturbed by plow or irrigation, the alkali is present at a considerable depth, being practically all concentrated in a particular zone. The series cited below was obtained from a point above the line of the ditch, and in consequence had never been irrigated, and further because of this no attempts at cultivation had ever been made.

SAMPLES FROM UNCULTIVATED PORTION OF HESPER FARM.

Lab. No.	Depth in inches.	Sodium sulphate. Per cent.	Alkalinity in terms of sodium carbonate. Per cent.	Moisture. Per cent.
359	0- 12	0.016	0.025	3.40
360	12- 24	0.006	0.021	4.30
361	24- 36	Trace	0.032	3.50
362	36- 48	0.015	0.021	3.50
363	48- 60	0.045	0.017	....
364	60- 72	0.077	0.014	....
365	72- 84	0.094	0.021	....
366	84- 96	0.123	0.014	....
367	96-108	0.104	0.014	....
368	108-120	0.115	0.025	....
369	132-144	0.288	0.021	....
370	144-156	0.379	0.017	....
371	156-168	0.737	0.010	....
372	168-180	0.780	0.017	....
373	180-192	0.745	0.014	....
374	192-204	0.605	0.017	....
375	204-216	0.574	0.014	....
376	216-228	0.458	0.010	....

With the advent of irrigation, the salts, usually deeply located, begin to rise to the surface. The water table formerly many feet deep approaches nearer and nearer to the surface, and of course brings the soluble salts with it.

An example illustrating the rise of the ground water may not be out of place here. In 1882, Mr. Hiram Abshire, whose ranche is near the middle of the valley, dug a well finding water at a depth of thirty-one feet; in September, 1897, fifteen years

later, the water had risen to within six feet of the surface. This is but one of many similar cases.

Samples taken from fields located on opposite sides of the main ditch show the zone of concentration of the soluble salts to be considerably deeper above the ditch than below it, and this is true even though the fields have never been irrigated.

Irrigation has the effect of concentrating the salts at the surface, for of course that which the water dissolves in its downward course, is brought up by it again when it rises by capillary action to supply surface losses due to evaporation. When it in turn evaporates, its salts are left upon the surface.

The following examples illustrate strikingly this action:

ALFALFA FIELD, IRRIGATED, FAIR CROP.

Lab. No.	Depth in inches.	Sodium sulphate. Per cent.	Alkalinity in terms of sodium carbonate Per cent.
221	0–12	0.140	0.017
222	12–24	0.198	0.014
223	24–36	0.039	0.014
224	36–57	0.036	0.014
225	57–72	0.036	0.017
226	72–90	0.039	0.017

BLUE JOINT FIELD, UNIRRIGATED, USED FOR PASTURE. ACROSS ROAD FROM PREVIOUS LOCALITY.

Lab. No.	Depth in inches.	Sodium sulphate. Per cent.	Alkalinity in terms of sodium carbonate. Per cent.
228	0–12	0.043	0.017
229	12–24	0.063	Trace
230	24–36	0.130	0.017
231	36–57	0.150	0.010
232	57–72	0.160	0.017
233	72–90	0.166	0.017

An inspection of these tables will show that while there is more soluble matter in the unirrigated field than in the other, yet the relative amount in the upper portion of the soil is much greater in the irrigated field. In these two cases the field under irrigation, presumably at the outset identical with the other, has concentrated in the first twenty-four inches seven-tenths of the total soluble sodium sulphate contained within the soil to a depth of ninety inches; the samples from the unirrigated field show the presence of but fifteen per cent. of sulphate in the first

two feet of soil, when compared with the quantity present to a depth of ninety inches. The lesser total quantity of sulphate present is to be attributed to the influence of large crops of alfalfa, which must remove with other mineral matter large quantities of alkali salts. This influence is especially marked in the case of the alfalfa field of the Hesper Farm, where two hundred and fifty acres yield twelve hundred tons of alfalfa hay annually.

Within a few feet of this field, on the east, is a field completely destroyed by "alkali," yet not only is the alfalfa field yielding immense crops, but it bids fair to continue to do so as indicated by the low percentage of alkali salts in the soil as shown in the following section:

HESPER FARM, ALFALFA FIELD.

Lab. No.	Depth in inches.	Sodium sulphate. Per cent.	Alkalinity in terms of Sodium carbonate. Per cent.	Water. Per cent.
377	0–12	0.012	0.017	11.50
378	12–24	0.004	0.021	11.70
379	24–36	0.015	0.028	12.60
380	36–48	0.013	0.025	.....
381	48–60	0.013	0.025	19.00
382	60–72	0.019	0.039	.....
383	72–84	0.031	0.039	19.50
384	84–96	0.054	0.032	.....
	Water.			

Where the soil is underlain with gravel, thus affording natural underdrainage, the alkali does not rise to the surface.

This condition exists with a number of ranches in the valley, and these are singularly free from alkali.

The best method for combating the evil would appear to be underdrainage, but land is so cheap that the expense of such a remedy could not be met. Careful surface flooding, economical use of water and intelligent cropping, are the remedies in the hands of the farmer, and properly employed will solve the problem.

THE MONTANA EXPERIMENT STATION,
BOZEMAN, MONTANA.

A CHEMICAL STUDY OF WHEAT.

By G. B. Frankforter and E. P. Harding.

Received May 1, 1899.

WHEAT, from its great commercial importance, has been made the subject of a large number of chemical discussions. As a result of these investigations, much has been learned concerning its chemical composition, and several hitherto new substances have been described. The extreme difficulty, however, in obtaining these new compounds, together with their non-crystallinity, leaves some doubt as to the actual existence of some of them.

One of the objects which presented itself, in beginning this paper, was to verify, if possible, the existence of tritisecalin and cerealin[1] and, if present, to isolate them. While the desire still exists, the numerous and perhaps less formidable questions which arose as the work progressed, led us somewhat from the original aim.

From an approximate analytical standpoint, wheat has been repeatedly examined. Konig[2] has made an exhaustive examination of the European varieties, while Richardson[3] has carefully examined those of our own states and Canada. Throughout the whole of these analyses, only water, oil, carbohydrates, albuminoids and ash were estimated, together with the weight of the average wheat grain.

From over two hundred analyses, Richardson obtained the following averages:

	Water.	Oil.	Carbohydrates.	Fiber.	Albuminoids.	Ash.
Per cent.	10.27	2.16	71.98	1.80	11.95	1.84

The average weight of 100 grains was 3.638 grams.

WHEAT OIL.

As above indicated, the quantity of oil in wheat has often been determined; but so far as we have been able to find, the oil itself has not been thoroughly studied. At the time of the beginning of this paper, the enormous quantities of wheat germ from the great mills of Minneapolis, had little or no value. It seemed important, therefore, that some commercial value should be found for this part of the wheat. As is well known, the germ

1 *Compt. rend.*, **37**, 775; **38**, 505; **42**, 1122; **48**, 431.
2 Nahrungs und Genussmittel.
3 *Am. Chem. J.*, **6**, 302.

of the wheat contains a very large per cent. of the oil, which was, therefore, obtained from that source.

Nowithstanding the fact that the oil has been determined in the germ and bran of the mills of Minneapolis, the improved methods of milling made it of interest to repeat some of these determinations. According to these analyses,[1] the germ was divided into three distinct parts, varying materially in the amount of oil they contain. The following per cents. of oil were obtained:

	Per cent. of oil.
First germ	9.35
Second germ	15.6
Third germ	13.75

According to the best milling authorities here, no such distinction can be made at the present time. Several analyses of all the different samples which could be obtained, ran between eleven and twelve per cent. of oil. The average of all these analyses was 11.6 per cent.

In the separation of the oil from the germ, several methods were tried. The simple extraction with ether was finally adopted as giving best results. The oil, when first extracted from the germ, has a golden-yellow color and a characteristic odor of freshly ground wheat. It has a specific gravity of 0.9292 at 15° C., and 0.9374 at 0°C. At 15°, it begins to change in appearance, becoming milky, and at 0° it becomes a cloudy semisolid. Warmed at 100° C., the above-mentioned odor is very pronounced and the oil changes color, becoming reddish brown. It is very soluble in ether, petroleum ether, chloroform, carbon disulphide, acetone and comparatively so in methyl and ethyl alcohols. It cannot be regarded as a drying oil, as it loses slightly in weight after exposure to the air for a month. After that time, the weight appears perfectly constant. The following table will show that the oil can not even be regarded as a semi-drying oil. For the sake of comparison, duplicate drying experiments were made with pure linseed oil.

GAIN (+) AND LOSS (—) IN PARTS PER HUNDRED AFTER DRYING AT THE ORDINARY TEMPERATURE THE INDICATED NUMBER OF DAYS.

	Number of days.						
	5	10	15	20	25	30	35
Linseed oil	0.037	0.13	0.28	1.74	4.82	7.55	7.94
Wheat oil	0.037	0.077	0.15	0.24	0.30	0.37	0.37

[1] *Am. Chem. J.*, **6**, 388.

	Number of days.							
	40	45	50	55	60	65	70	75
Linseed oil	7.94	7.94	7.90	7.90	7.90	7.95	7.95	8.43
Wheat oil	0.41	0.42	—0.22	—0.26	—0.28	—0.28	—0.30	—0.42

The variation in the results between thirty-five and fifty days is undoubtedly due to outside physical conditions. Under exactly the same temperature, linseed oil will more than likely increase in weight uniformly, until the maximum of 8.5 per cent. is reached. Wheat oil, as indicated in the above table, can not even be regarded as a semidrying oil. Although a slight increase in weight was indicated during the first forty-five days, the loss by weight which followed, a little more than counterbalanced the gain. The oil, at the end of the above-stated time, appeared almost unchanged.

VISCOSITY OF WHEAT OIL.

The viscosity of wheat oil was taken at the various temperatures indicated below, as compared with pure rape oil. The following is a ratio between the two oils:

Temperature	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Wheat oil	1.43	1.81	2.57	1.92	1.67	1.48	1.40	1.39	1.27	1.20	1.14

While rape oil, which was taken as unity, was found to vary quite uniformly with increase of temperature, wheat oil increased more rapidly from 0° to 20° than from 20° to 100° C., making the maximum ratio between the two oils at 20° C. This ratio may be represented by the following curve in which the temperature is the abcissa, and the relative viscosity, the ordinate:

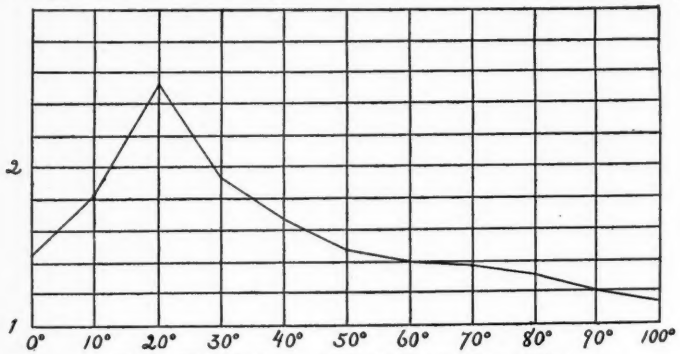


Fig. 1.—Viscosity Curve of Wheat Oil, Rape Oil as Unity.

INDEX OF REFRACTION.

The index of refraction of wheat oil was taken at different temperatures by the Pulfrich refractometer. The following is a comparison of wheat oil with corn and linseed oils:

Temperature	20°	30°	40°	50°	60°	70°	80°
Corrected index of wheat oil	1.47878	1.47544	1.47181	1.46858	1.46459	1.46161	1.4586
Corn oil	1.47789	1.47436	1.47053	1.46728	1.46360	1.46002	1.45642
Linseed oil	1.48558	1.48072	1.47730	1.47329	1.46954	1.46697	1.46281

The above readings were taken with wheat oil, just as it was obtained from the germ, by extracting with ether. The oil, therefore, contained all the substances occurring in the germ, which are soluble in ether. Some of these, it was found, could be removed by redissolving in ether and evaporating rapidly, while nearly all of these substances, including the paracholesterol, were removed by treating with alcohol. The oil thus purified had changed its properties slightly. The refractive index had changed somewhat, giving at a temperature of 20°, 30°, and 40° C., corrected indices of 1.48325, 1.47936, and 1.47447 respectively.

THE ABSORPTION SPECTRUM OF WHEAT OIL.

So far as we can learn, very little has been done on the absorption spectra of the oils. Several attempts have been made to classify the oils with regard to their absorption bands, but as these bands are in many cases due to impurities in the oil, the classification is a rather imperfect one. According to Vogel,[1] who briefly studied a few of the organic substances, these bands are nearly always due to the presence of foreign matter, as chlorophyl or other coloring substance, for by removing these coloring substances, the absorption bands disappear. This statement seems to be true within certain limits, in the case of the oils. A few of the oils undoubtedly owe their spectra to chlorophyl or some other coloring-matter. Many of them, however, have spectra entirely independent of foreign substances. Doumer,[2] in a spectral examination of some of the oils, divided them into four distinct classes which were represented by the following characteristics:

[1] Vogel's Spectralanalyse, Vol. I.
[2] *Analyst* (*1885*), 148.

Class I, oils showing bands due to chlorophyl.

Class II, oils without absorption bands.

Class III, oils absorbing the chemical rays of the spectrum, the red, orange, yellow and a part of the green remaining unchanged.

Class IV, oils showing absorption bands in different parts of the scale.

According to this classification, linseed, mustard and rape oils belong to Class III. A glance at the following spectra will indicate that linseed together with wheat and corn oils belong to Class IV. We have found that the spectrum depends largely upon the length of the tube used. Thus with proper length tubes these three common oils may belong to Class III, while with different tubes they may be regarded as members of Class IV. It seems evident, if this classification is to be used, that the length of the tube must be taken into consideration. Thus, wheat oil, with a 200 mm. tube, gives a rather indistinct spectrum, while with a 100 mm. tube, the spectrum is characterized by two very distinct bands, as seen below. Corn and linseed oils, with the same length tube, appear to belong to Class III. However, with a tube double the length, they undoubtedly belong to Class IV as will be seen by the following charts:

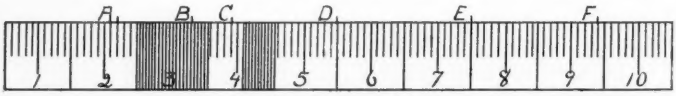


Fig. 2.—Wheat Oil.

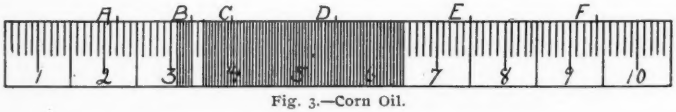


Fig. 3.—Corn Oil.

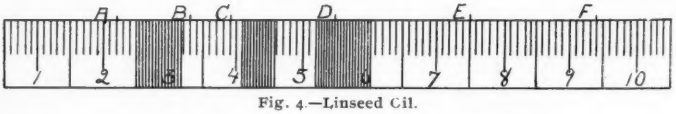


Fig. 4.—Linseed Oil.

SOLUBILITY OF WHEAT OIL.

Solvent.	Solvent required to dissolve one gram of oil. cc.
Ether	1
Chloroform	1
Absolute Alcohol	30
Ninety per cent. alcohol	250

Some difficulties were at first experienced in determining the solubility, owing to the fact that a small quantity of unsaponifiable substance was soluble with difficulty in absolute, and almost insoluble in ninety per cent., alcohol. The oil was at first purified by dissolving in a small quantity of absolute alcohol and filtering. The tests were made on the oil thus purified.

SAPONIFICATION VALUE OF WHEAT OIL.

The saponification value of wheat oil was determined according to Köttstorfer's method which represents the number of milligrams of potassium hydroxide required to saponify one gram of the oil. The results obtained agree best with the values obtained from the semidrying oils, notwithstanding the fact that the drying experiments would not permit it to be classed in that group.

The following is the result of four determinations as compared with the results obtained from typical semidrying oils:

	Milligrams of KOH required to saponify one gram of oil.		
	Minimum.	Maximum.	Mean value.
Wheat oil	187.40	190.27	188.83
Pumpkin seed oil	186.6	189.81	188.21
Maize oil	188.00	193.4	190.7

In these determinations, freshly extracted oil was used, inasmuch as oil extracted for some time gave varying results.

THE IODINE VALUE.

The iodine value of wheat oil was determined according to Hübl's method. Three determinations gave the following results:

I. 0.1998 gram of the oil absorbed 232 milligrams of iodine.

II. 0.1866 gram of the oil absorbed 216 milligrams of iodine.

III. 0.1505 gram of the oil absorbed 174 milligrams of iodine.

	Per cent. of iodine found.		
I.	II.	III.	Average.
116.16	115.75	115.03	115.64

Pumpkin seed gave a mean of ..... 121.

Maize oil gave a mean of ..... 122.27[1]

THE ACID VALUE.

The acid value of wheat oil was determined by the common method of titrating a known quantity of the oil with decinormal alcoholic potassium hydroxide. Three determinations gave the following results:

I. 1.594 grams of the oil required 0.066 gram of potassium hydroxide.

II. 1.5616 grams of the oil required 0.06284 gram of potassium hydroxide.

III. 1.268 grams of the oil required 0.05145 gram of potassium hydroxide.

	I.	II.	III.
Acid value	41.4	40.2	40.5

DETERMINATION OF GLYCEROL.

Glycerol was determined by the oxidation process, that is, the oxidation of glycerol to oxalic acids by means of alkaline potassium permanganate according to the following reaction:

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O,$$

and the estimation of oxalic acid, from which glycerol can be determined. The method as worked out by Benedict and Zsigmondy was used, and is briefly as follows: Two or three grams of the oil were saponified with potassium hydroxide in methyl alcohol. The alcohol was removed by evaporation, the soap dissolved in hot water and decomposed by hydrochloric acid. The whole mass was then warmed until the fatty acids had collected on the surface. These acids were filtered off and the filtrate carefully neutralized with potassium hydroxide. Ten grams of the hydroxide were now added and an excess of permanganate, or until the liquid appeared blue or dark red. The excess of permanganate was destroyed by sulphurous acid and the whole solution again filtered. The filtrate obtained was acidified with acetic acid, diluted to a liter, heated to the boiling-point, and the oxalic acid precipitated by calcium chloride.

[1] This Journal, **20**, 948.

From the calcium oxalate formed, the amount of oxalic acid and hence the per cent. of glycerol can be calculated. Five analyses gave the following results:

I. 2.7696 grams of oil gave 0.2024 gram of glycerol.
II. 2.9074 grams of oil gave 0.2145 gram of glycerol.
III. 2.8778 grams of oil gave 0.2124 gram of glycerol.
IV. 2.1640 grams of oil gave 0.1557 gram of glycerol.
V. 3.4940 grams of oil gave 0.2631 gram of glycerol.

	I.	II.	III.	IV.	V.
Per cent. glycerol.....	7.34	7.29	7.38	7.2	7.53

DETERMINATION OF LECITHIN IN WHEAT OIL.

Frequent references have been made to the occurrence of lecithin in wheat, but no quantitative determinations have been made, so far as we can learn. As the base was apparently abundant in the oil, determinations were made, using the common phosphoric acid method. A known quantity of the oil was saponified with a concentrated solution of potassium hydroxide and heated on a water-bath until all the alcohol had been removed. The soap thus formed was decomposed with hydrochloric acid and the fatty acids filtered off. The filtrate, which contained all the phosphorus, was evaporated to dryness and fused with potassium hydroxide and potassium nitrate. From the fused mass the phosphoric acid was determined and the lecithin calculated. Two determinations gave the following results:

I. 23.1858 grams of oil gave 0.0697 gram magnesium pyrophosphate.

II. 27.4514 grams of oil gave 0.079 gram magnesium pyrophosphate.

	I.	II.
Calculated for lecithin	2.03	1.96

In making the above calculations, we have assumed that the lecithin was an oleyl rather than a stearyl ester. This assumption was made from the fact that in the analysis, little or no stearic acid was found in the oil. The formula used therefore, was

$$C_{42}H_{84}O_9NP.$$

PARACHOLESTEROL IN WHEAT OIL.

Cholesterol was first obtained from wheat by Ritthausen.[1] By extracting the gluten, as well as the fats in wheat with ether, he obtained, on evaporating off the ether, a crystalline substance which had very similar properties to the cholesterol of Beneke.[2]

It was afterwards regarded as identical with an isomeric form of cholesterol discovered by Hesse,[3] and called phytosterol.

In the beginning of our work on this substance, we obtained a melting-point which compared so well with phytosterol, that, with Koenig,[4] we regarded the two substances as identical.

However, after carefully recrystallizing several times, the melting-point had risen enough to make it doubtful if the substance in wheat were phytosterol. The melting-point of phytosterol, as given by Hesse and others, is 132°–133°C., while the purified substance from wheat, melted at 134°–135°C. A much greater difference, however, was observed in a comparison of the wheat cholesterol with the common or animal cholesterol, the melting-point of which ranges from 140° to 148°C. These two substances, to neither of which wheat cholesterol belongs, were all which were known to the earlier authorities, and according to Maly,[5] these two substances were identical. However, later investigations seeem to prove beyond a doubt, that several different forms of cholesterol exist. Reinke and Rodewald[6] found in protoplasm of *aethalium septicum*, a substance to which, after examination, they gave the name paracholesterol. Later, Schulze and Barbieri[7] repeated much of the work which had previously been done, and showed that no less than five different isomeric forms of cholesterol existed, or two more than had heretofore been described. These isomeric forms, together with their melting-points and optical activities, are given in the following table:

1 *J. prakt. Chem.*, **88**, 145.
2 *Ann. Chem.* (Liebig), **122**, 249.
3 *Ibid.*, **192**, 175.
4 Koenig's Nahrungs- und Genussmittel, 3rd Auf., **2**, 461.
5 *Jahresber. d. Thierchem.*, (*1878*), 270,
6 *Ann Chem.* (Liebig), **207**, 229.
7 *J. prakt. Chem.*, **25**, 159.

ISOMERIC FORMS OF CHOLESTEROL.

Name.	Melting-point.	Optical Activity.	Authority.
Cholesterol	145°–146°	$(a)_D = -36.61$	Hesse
Phytosterol	132°–133°	$(a)_D = -34.2$	Hesse
Paracholesterol	134°–134.5°	$(a)_D = -28.88$	Reinke Rodewald
Caulesterol	158°–159°	$(a)_D = -49.6$	Reinke Rodewald
Isocholesterol	138°–138.5°	$(a)_D = +60$	Schulze

As will be seen from the above table, four of these forms of cholesterol are laevo-, while the fifth is dextrorotatory, thus affording a means of distinguishing between isocholesterol and the other members. In fact, the differences between the other members, taking into consideration the melting-points, are sufficient to readily distinguish between them. A glance at this table will enable us to identify the cholesterol in wheat as paracholesterol. The melting-points are exactly the same while the planes of rotation are almost the same, as will be seen by the comparison given below:

2.7 grams of paracholesterol gave $(a)_D$ 28.88, melting-point 134.5°.

1.7948 grams of paracholesterol gave $(a)_D$ 27.24, melting-point 134.5°.

1.3848 grams of wheat cholesterol gave $(a)_D$ 26.9, melting-point 134.5°.

Taking into consideration the variation in the plane of polarization obtained by Reinke and Rodewald with different amounts of paracholesterol, the results obtained with wheat cholesterol will check exactly with paracholesterol.

DETERMINATION OF PARACHOLESTEROL.

The methods given for the extraction of these isomeric forms of cholesterol are very much the same. The method in common use is as follows: The substance containing the cholesterol is first saponified with potassium hydroxide and the cholesterol extracted by ether. The ether usually dissolves some other substances besides the cholesterol. These impurities are removed by again treating with potassium hydroxide, again extracting with ether and finally recrystallizing from alcohol. Bömer[1] avoided this tedious process of evaporation, by extracting with

[1] *Ztschr. Unters. d. Nahrungs- und Genussmittel, (1898)*, 31.

ether from aqueous solution. This method was found objectionable, on account of the large quantity of ether necessary to obtain perfect extraction.

Raumer[1] used good clean beach sand after saponification, the object being to assist in both evaporation and extraction.

This method will give good results, provided the sand is clean. Juckenack and Hilger[2] suggest the use of sodium hydroxide instead of potassium hydroxide, and filter-paper instead of sand.

The above methods all give good results, the principal difference being in the time and material required. The method which we adopted, was that involving the saponification with alcoholic potassium hydroxide and extracting the dried soap with ether in a Soxhlet extractor. Five analyses gave the following results:

I. 20.0000 grams of oil gave 0.5216 gram of paracholesterol.
II. 9.3380 grams of oil gave 0.2209 gram of paracholesterol.
III. 10.3332 grams of oil gave 0.2510 gram of paracholesterol.
IV. 10.1314 grams of oil gave 0.2510 gram of paracholesterol.
V. 110.3000 grams of oil gave 2.7573 grams of paracholesterol.

	Per cent.				
	I.	II.	III.	IV.	V.
Calculated for paracholesterol	2.6	2.37	2.43	2.46	2.49

THE ELAIDIN METHOD.

Among the new methods tried, was one which involved the elaidin reaction, and which, carefully carried out, gave fairly good results. The method of operating was as follows: About twenty grams of the oil were transferred to a tall beaker, ten grams of mercury added, then ten cc. of strong nitric acid, drop by drop. The temperature was kept between 8° and 10°, on account of the violent reaction between the mercury and the nitric acid at a higher temperature. When the mercury had quite dissolved, the beaker was gently warmed, in order to remove the excess of oxides of nitrogen. The whole mass was then treated with an excess of alcoholic potassium hydroxide, evaporated to dryness on a water-bath, and extracted with ether On evaporating off the ether, paracholesterol was obtained in comparatively pure form. By recrystallizing from alcohol, a very pure form was obtained.

[1] *Ztschr. angew. Chem.*, (*1898*), 555.
[2] *Arch. Pharm.*, **236**, 367.

Two determinations gave the following results:

I. 25.64 grams of oil gave 0.464 gram of paracholesterol.

II. 15.792 grams of oil gave 0.3474 gram of paracholesterol.

	Per cent. I.	II.
Calculated for paracholesterol.....	1.8	2.2

Although the paracholesterol was obtained in a comparatively pure form by this method, considerable difficulty was experienced in evaporating to dryness, several hours being required. It was also observed, that when more than the above-mentioned amount of nitric acid was used, the quantity of paracholesterol was diminished. Thus with double the quantities of nitric acid and mercury only four-tenths per cent., and with three times the quantity of acid and mercury only a trace, of the paracholesterol was obtained. Just why this diminution in the quantity of paracholesterol should occur, is not definitely known. The probabilities are, however, that it forms, with the excess of nitric acid, a nitrolic acid according to the common reaction.

THE ESTIMATION OF ARSENIC IN PARIS GREEN.

BY THORN SMITH.

Received May 6, 1899.

IN selecting a method for the analysis of the common insecticide, Paris green, some difficulty was encountered in finding one suitable to the ordinary requirements of rapidity and corresponding accuracy. In fact the only methods of which record was found are as follows:

First, by direct precipitation of the arsenic as magnesium pyroarsenite by means of magnesia mixture or what would be embodied in the same method, a first separation of the sulphides of arsenic and copper, by means of hydrogen sulphide, and a consequent tedious separation of the arsenic from the copper by means of ammonium sulphide, followed by the precipitation of the arsenic as at first. This latter modification is given in the majority of text-books, which mention the subject at all. Its objection is the large amount of time consumed in the operation and the danger of loss in separating the arsenic from the copper.

The second method known as the "Pearce" or "McCay" method is perhaps just as difficult with the added objection that such small amounts of the material are permitted in the pro-

cess, that errors are sure to creep in. The Paris green is fused with sodium carbonate and potassium nitrate, extracted with water, and the sodium arsenite in the water solution oxidized to the arsenate by nitric acid. The arsenate is then precipitated by silver nitrate, volumetrically. The amount of silver precipitated is to the arsenic as 108 is to 25. This method is undoubtedly well adapted to material containing but small amounts of arsenic, but where from forty to sixty per cent. is arsenic not more than two-tenths of a gram can be handled, and even then the precipitate is so bulky that inconvenience is caused. A large amount of the silver solution is also required. Either of the above will undoubtedly give exact results in the hands of an experienced analyst, but when the attempt is made by the ordinary student, woeful results generally follow and discouragement naturally attends.

In presenting the following method I may have nothing new; in fact it may be a well-known method but at least none of the text-books at my command nor any of the standard authorities mention it. I have taken advantage of well-known reactions, and in part have used volumetric methods given by Sutton. Owing to the variable composition of Paris green, one reaction does not fit all cases but the composition and degree of oxidation of the essential elements are the same. If a copper salt be boiled with a slight excess of sodium hydroxide, in the presence of a reducing agent, cuprous oxide is formed. Therefore, if the arsenite of copper be boiled with sodium hydroxide, cuprous oxide is formed by the reducing action of the arsenite and at the same time a portion of the arsenite is oxidized to the arsenate, in this case, sodium arsenate. The latter being soluble can be filtered from the precipitated cuprous oxide, and this solution being alkaline, can be concentrated without loss. If this concentrated solution be strongly acidified with hydrochloric acid and, while still warm, an excess of potassium iodide be added, the arsenate is wholly reduced to the arsenite. The reaction is complete in a few minutes. The acid solution now contains a large amount of free iodine which can be consumed by carefully adding a dilute solution of sodium hyposulphite, followed by the addition of sodium carbonate until the solution is neutral. An excess of the bicarbonate is then added and the

solution titrated against tenth-normal iodine, using starch as an indicator.

As finally adopted the following method is used in this laboratory:

Two grams of the Paris green are weighed out, about 100 cc. of water added, and two grams of sodium hydroxide. The solution is brought to a boil and boiling continued for a few minutes. It is then allowed to cool to room temperature and the solution made up to 250 cc. The well-shaken liquid is filtered through a dry filter and fifty cc. taken for the analysis. This portion equal to four-tenths gram is concentrated to about one-half its volume and allowed to cool to about 80° C. An equal volume of strong hydrochloric acid is then added accompanied by three grams of potassium iodide and the whole allowed to stand for ten minutes (longer is not necessary). The deep red solution is slightly diluted with water to dissolve the precipitate caused by the potassium iodide and a dilute solution of sodium hyposulphite added until the color just disappears. This solution is then made neutral by the addition of dry sodium carbonate and finally an excess of sodium bicarbonate is added. Tenth-normal iodine is dropped in and the end-reaction noted by starch solution.

I have found it easier in calculating results to use a solution of iodine such that one cc. equals 0.005 gram of arsenic trioxide, instead of the exactly tenth-normal solution, one cc. of which equals 0.00495 gram. The number of cubic centimeters of such a solution multiplied by one and one-fourth equals the per cent. of arsenic trioxide in the Paris green. Two grams are taken for the assay and four-tenths taken for the operation, owing to the fact that generally but slightly less than fifty cc. are required for the titration and thus a second filling of the burette is avoided, which would be necessary were five-tenths gram taken. Working by this method an analysis can be made in less than one hour whereas by the other methods several hours or days are required. If desired, the copper as cuprous oxide can be dissolved and titrated against potassium cyanide by standard methods. The end-reaction in the arsenic titration is sometimes difficult owing to the large amounts of foreign salts in the solution. A deep red color is produced as the titration

proceeds but the unmistakable blue can easily be seen after a few trials.

Working by this method I have obtained duplicates within 0.05 per cent. which is certainly accurate enough for all practical purposes. My results have also checked the gravimetric methods very closely.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF IDAHO,
April 29, 1899.

THE DETERMINATION OF SULPHUR IN BITUMENS.[1]

BY S. F. AND H. E. PECKHAM.

Received June 13, 1899.

THE paper read by Mr. E. H. Hodgson, which appeared in the November (1898) number of this Journal, was read by us with great interest. It is evidently intended to be a description of a fair comparative test of the value of the several methods used for the determination of sulphur in the different varieties of bitumen examined.

We wish to call attention to a number of unrecognized, or at any rate unmentioned conditions, which, in our opinion, rendered the results, given by Mr. Hodgson, variable, and to some extent unreliable.

Of the specimens selected for analysis, it is to be said, that the two specimens called "Trinidad Lake" and "Trinidad Lake refined" are very peculiar substances. They, in common with all other Trinidad pitch, consist of a mixture of bitumen, mineral matter, organic matter that is not bitumen, and a considerable proportion of ferric and aluminic oxides, that are combined with organic radicals to form complex salts. There are sound reasons for believing that some of the sulphur is free, some of it in combination with iron as pyrites, in an extremely minute state of division, and some of it in combination as thio-salts, in which it performs a linking rather than saturating function.

There can be no question that the action of nitric acid on this complex mixture of various substances results in the formation, not only of sulphuric oxide, but of other oxides of alumina and iron, that will almost certainly form double barium salts with sulphuric acid, that are nearly or quite as insoluble as pure ba-

[1] Read at the June Meeting of the New York Section.

rium sulphate, and consequently follow, or accompany the barium sulphate, even to the final weighing.

Many years ago one of us precipitated alumina as a double barium and aluminum sulphate, from a solution of potash alum. The potash alum had been mixed, dry with barium chloride, and, as is remembered, with the potash alum largely in excess, as a puzzling problem in qualitative analysis. On attempting to dissolve the mixed salts, a barium alum or double sulphate of barium and aluminum remained undissolved. This reaction indicates why it is of importance that the oxides of iron and alumina should be removed from the solution before the barium chloride is added.

The specimen denominated "Trinidad crude" and further described as "crude asphalt from Hadley's diggings, about one mile from Trinidad Lake; it is known as 'iron pitch,' being the hardest asphalt found in Trinidad," is not asphalt at all, but is a residue from the natural distillation of the pitch by jungle fires. It is found in small masses, and in small quantity, all over the deposit, both within and without the lake, and is uniformly rejected as rubbish. It has been subjected to such a temperature that all of the water has been expelled, and the whole mass melted and brought to a condition of semifluidity. Apparently the sulphur is in part expelled, and that which remains is evidently brought into such a condition that the nitric acid process fails to produce the reaction essential to the formation of double salts, as the results of the analyses by the four processes used by Mr. Hodgson are essentially alike. The results obtained from Cuban, Alcatraz, and California asphaltum are evidently subject to the same criticism as the Lake pitches, in a less degree.

The deflagration method, as described in Mr. Hodgson's paper, is not the method used by the authors. We never used a porcelain crucible; first, for reason of its form, and second, for reason that the fluxes used will react with the porcelain, making it impossible to determine the iron, alumina, and silica in the assay.

We have modified to a slight degree our method of procedure, as experience has suggested, until finally we have weighed out such an amount of the assay as will represent about five-tenths gram of bitumen. This is very thoroughly mixed with fifteen grams each of pure and dry sodium carbonate and potassium

nitrate. The salts are first thoroughly pulverized and mixed in an unglazed porcelain mortar. Two-thirds of the mixture are then removed to a sheet of glazed paper. The assay is then mixed in the mortar with the flux in the most thorough manner and then removed to a second sheet of glazed paper. The mortar is then carefully rinsed with the remaining flux in two successive portions. The whole of the flux and assay are then brought to a uniform mixture on the glazed paper. The mixture is then placed, small portions at a time, into a two-ounce platinum crucible, heated to dull redness. No fusion with a blast-lamp is necessary, as the assay is in quiet fusion when the last portion has deflagrated. A large excess of flux lessens the violence of the combustion and also lessens the liability to loss by spattering.

The contents of the crucible are then dissolved by allowing it to remain covered with water in a beaker, preferably over night. When the solution is complete, the crucible is washed off and the contents of the beaker rendered acid with hydrochloric acid. The solution is then evaporated to dryness over a water-bath, the silica dehydrated, moistened with hydrochloric acid, treated with water and the silica filtered off, ignited, and weighed. The solution is rendered alkaline with ammonia, boiled until the excess of ammonia is removed, and the precipitate of iron and alumina dried and weighed as usual. The iron may be found in another portion with potassium permanganate and the alumina determined by difference. Lime may be determined as oxalate if desired.

The solution, freed from silica, iron, alumina, and lime, is brought to a boil, acidulated with hydrochloric acid, and the sulphuric acid precipitated with barium chloride, added in small portions at a time from a pipette. This method for the determination of sulphur is susceptible of great accuracy, if *conducted with care*. It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant.

We have not found the slightest difficulty in bringing out concordant results to the second place of decimals, and sometimes to the third. The method has also been proved presumably correct, by reason of determinations made by first estimating the

sulphur in a very pure asphalt and then in the same asphalt to which a weighed quantity of pure sulphur had been added dry. The results showed the amount of sulphur in the pure bitumen plus the amount of pure sulphur added.

Dr. William C. Day, of Swarthmore College, has lately used this method for determining sulphur in the natural and artificial gilsonites that he has had under examination. He has kindly given me the results that he has obtained in several analyses of these substances, which fully illustrate of what the method is capable in skilful and sympathetic hands. We give his results below.

	Weight taken. Grams.	$BaSO_4$ obtained. Gram.	Sulphur. Per cent.
Utah Gilsonite.			
I	2.7111	0.0474	0.0024
II	2.1651	0.0390	0.0025
III	2.1017	0.0388	0.0027
Fish and Wood Asphalt.			
I	2.0218	0.0136	0.0009
II	1.9988	0.0114	0.0008
Wood Asphalt.			
I	1.9753	0.0134	0.0009
II	1.3777	0.0095	0.0009
Fish Asphalt.			
I	2.0402	0.0287	0.0019
II	1.9954	0.0276	0.0019
Indian Territory Asphalt.			
I	2.1676	0.2216	1.40
II	2.2410	0.2238	1.37

These results are sufficiently concordant for any purpose, and are given in preference to our own, although we have found no difficulty in obtaining equally satisfactory figures, both with pure bitumens and mixtures of bitumens with pure sulphur.

This method is simple, reasonably rapid, and accurate, does not require complex and expensive apparatus and, what is especially to be noted, furnishes a ready means for the determination in the same solution of other constituents of most solid bitumens, the correct estimation of which is often of the greatest importance.

It is to be further noted that in these analyses about two grams, more or less, are taken for an assay. These materials are all exceptionally low in sulphur. It is therefore necessary to take a larger portion than is usually found advisable in the use of this process, and when so much of the asphalt is burned it becomes absolutely necessary to use a larger proportion of the flux, otherwise some of the assay will escape oxidation.

Note.—In the discussion that followed the reading of this paper, it was claimed that mercaptans and similar constituents of bitumens could not be oxidized by this method. It has not yet been shown that mercaptans and similar sulphur compounds exist as constituents of crude bitumens in such amount as to be worthy of consideration in this connection. This method is not recommended as superior to the method of Carius in ultimate research, but is recommended for the determination of sulphur in solid and semisolid bitumens for practical purposes.

May 1, 1899.

[A CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

A NEW METHOD FOR THE DIRECT DETERMINATION OF ALUMINA IN PRESENCE OF IRON, MANGANESE, CALCIUM, AND MAGNESIUM.

BY WILLIAM H. HESS AND E. D. CAMPBELL.

Received June 17, 1899.

THE method most commonly used for the determination of alumina in presence of iron, manganese, calcium, magnesium, and phosphoric acid, is the indirect method in which the iron, alumina, and phosphoric acid are obtained together as a combined precipitate with ammonia. The alumina is taken as the difference obtained by deducting the weight of phosphorus pentoxide and ferric oxide as determined in separate samples. While the determinations of phosphoric acid, as well as the volumetric estimation of iron are satisfactory, an error may be introduced by careless ignition of the mixed oxides, since ferric oxide may be more or less converted to magnetic oxide (Fe_3O_4), with loss of oxygen; while in the calculations all the iron is figured as ferric oxide. Any error arising from careless ignition, from failure to perfectly wash the precipitate, or from an imperfect separation of other substances present as calcium, zinc,

nickel, etc., goes to increase or decrease the percentage of alumina found.

Among the direct methods for determining alumina, the best known and most used are the alkali method and the thiosulphate method of Wöhler. Neither of these succeed satisfactorily when only traces of alumina are present with iron. Neither the potassium cyanide method nor the basic nitrate method of Beilstein and Luther seem to have become popular. These methods, as well as many others that have been worked out, either require special expensive platinum apparatus or much attention to detail to obtain the correct conditions. In short, the present direct methods for estimating alumina are laborious, and too uncertain in their accuracy to pay for the heavy labor entailed, and consequently have not as yet displaced the simple though somewhat uncertain indirect method.

A method for the direct determination of alumina in presence of other substances commonly occurring with it, which is accurate, simple and rapid, would seem to be of great practical value, especially to those chemists connected with the iron ore industry, with cement and other clay industries, as well as in general mineral analysis.

While engaged in trying to modify the old alkali process so as to make it more satisfactory, experiments were carried on with a view of finding some reagent which would quantitatively precipitate alumina without precipitating iron. Recourse was taken to the organic bases for a suitable reagent for this purpose.

The well-known ammonium base, phenylhydrazine, which has proved of such great value in establishing the chemistry of the sugars, was found to be the most satisfactory of the many organic bases tried for the precipitation of alumina. As a base it is somewhat weaker than ammonia. It precipitates aluminum from its solutions quantitatively as the hydroxide without a trace of the precipitate being redissolved in excess of the precipitant. Phenylhydrazine is, moreover, a strong reducing agent, quickly reducing iron from the ferric to the ferrous state, thus playing a double rôle of usefulness in the separation of iron from alumina.

METHOD OF ANALYSIS.

A convenient sample to be analyzed is weighed out and

obtained in solution preferably as the chloride in the usual way. To a convenient bulk of solution, 200 to 300 cc. heated to near the boiling-point, dilute ammonia is added slowly as long as the precipitate formed just redissolves with readiness. A neutral, saturated solution of ammonium bisulphate[1] is added, drop by drop, with stirring to this hot and nearly neutral solution, until it becomes colorless, showing the complete reduction of the iron. To the hot solution now smelling strongly of sulphur dioxide, one or two cc. of phenylhydrazine are added. If this amount of phenylhydrazine causes a permanent precipitate, then a few drops more of phenylhydrazine are added to insure complete precipitation of the alumina. If one to two cc. of phenylhydrazine do not produce a permanent precipitate, it is economical, after adding this amount of phenylhydrazine, to add dilute ammonia carefully, drop by drop, to a just perceptible permanent precipitate, and then complete the precipitation by adding a few drops more of phenylhydrazine. The precipitate, consisting of aluminum hydroxide and aluminum phosphate, is filtered out on an ordinary filter and washed with warm water containing a small amount of phenylhydrazine bisulphite. This washing solution is prepared as follows: To a few cubic centimeters of phenylhydrazine in a beaker, a saturated water solution of sulphur dioxide is added gradually until the precipitate of phenylhydrazine sulphite, which at first separates out in crystals, is redissolved to a yellow solution. If, after a few minutes, an odor of sulphur dioxide is perceptible, a few drops of phenylhydrazine are added to neutralize this excess of sulphurous acid. This concentrated solution of phenylhydrazine bisulphate, if well stopped, will keep indefinitely. Five to ten cc. of this to 100 cc. of water is an efficient strength of solution for washing the precipitate of alumina. The washing with this warm solution is continued until the washings give no test for iron with ammonium sulphide. A drop or two of phenylhydrazine is added to the filtrate with stirring to see if the precipitation has been complete. If chlorides of metals other than iron be present, the washing must be continued until the washings are free from chlorine. The presence

[1] (This solution of ammonium bisulphite is made by passing sulphur dioxide into a cooled solution of ammonia (1 : 1) until the solution becomes yellow. It serves the purpose here, not only of reducing the iron, but the excess of sulphurous acid unites with the phenylhydrazine added, to form a salt which acts as a most efficient agent for keeping the iron reduced and thus prevents its precipitation with the alumina.)

of chlorides of volatile bases will do no harm in the ignition of alumina.

The precipitate together with the filter is placed in a platinum crucible, dried and the filter charred at a low temperature. After the filter is completely burned, the ignition is continued at a bright red heat to constant weight. Care is taken to weigh quickly with the cover on the crucible, since both the phosphate and oxide of aluminum are very hygroscopic. A second ignition and weighing is always necessary. This precipitate of alumina carries all the phosphorus pentoxide so that the weight of alumina is found by subtracting the weight of phosphorus pentoxide found in a separate sample.

Chromium is quantitatively precipitated by phenylhydrazine, and may thus be separated from iron with great readiness. Neither calcium, magnesium, manganese, cobalt, or nickel is precipitated.

GRAVIMETRIC METHOD FOR IRON.

If a gravimetric estimation of the iron is desired, it has been found to be most expedient to add ammonium sulphide to the filtrate in case there is no other metal present that will be precipitated by this reagent. The sulphide of iron thus formed is filtered out, and without washing is redissolved in dilute hydrochloric acid. From this hydrochloric acid solution the iron is estimated in the usual way with ammonia after oxidation with nitric acid. It may under some circumstances be desirable to separate the iron and alumina by means of ammonia or as basic acetate, to get rid of other metals before attempting their specific separation by means of phenylhydrazine.

SEPARATION AND ESTIMATION OF PHOSPHORIC ACID.

Since the aluminum hydroxide precipitated with phenylhydrazine carries all the phosphorus pentoxide with it that is present in the solution, this method may be conveniently used for its separation. If the alumina present in the mineral is not sufficient to carry all the phosphoric acid as the normal phosphate, an excess of a known solution of aluminum chloride is added. The alumina is then separated by the above method. If only the phosphoric acid is desired, this precipitate may be dissolved in nitric acid and the phosphoric acid may be deter-

mined in the usual way. Or the precipitate may be ignited and weighed, thus giving the combined weight of alumina added, of alumina in the mineral and of phosphoric acid in the mineral.

RESULTS ON KNOWN MIXTURES.

Mixtures were made by Prof. Campbell's private assistant which were strictly unknown to the operator, and were subjected to the above method of analysis with results as recorded in the following table:

	Weight of iron taken. Gram.	Al_2O_3 taken. Gram.	P_2O_5 taken. Gram.	$P_2O_5 + Al_2O_3$ taken. Gram.	P_2O_5 and Al_2O_3 found. Gram.	Gain or loss. Gram.
(1)	0.7023	0.00664	0.00077	0.000741	0.000735	0.00006
(2)	0.2020	0.1343	0.00022	0.13452	0.1343	0.00022
(3)	0.059934	0.0105	0.00576	0.01581	0.0162	0.00039
(4)	0.3339	0.0966	0.01072	0.10732	0.1066	0.00072
(5)	0.6604	0.030	0.00577	0.03577	0.03570	0.00007
(6)	0.551	0.05152	0.01073	0.06225	0.06220	0.00005
(7)	0.527	0.0219	0.01073	0.03263	0.0330	0.00037
(8)	0.564	0.0644	0.00822	0.07262	0.0719	0.00072

A solution was prepared by dissolving one gram of calcium carbonate, 0.200 gram magnesium carbonate, 0.571 gram of ferric oxide, and one gram of manganous chloride, in hydrochloric acid. To this solution, 0.09016 gram aluminum oxide, and 0.05234 gram of phosphorus pentoxide was added. The combined weight of alumina and phosphorus pentoxide taken was therefore 0.1425 gram. The weight found was 0.1428 gram.

UNIVERSITY OF MICHIGAN,
June 15, 1899.

THE DETERMINATION OF ANTIMONY IN ORES.

BY THOMAS BROWN, JR.

Received May 9, 1899.

THE object of this paper is not to present new methods, but on the other hand the application of some very old ones which have been agreed upon by the buyers and sellers for determining antimony in ores, and which after trial have been proved to give more closely agreeing and satisfactory results than those formerly obtained by the many more widely used volumetric and gravimetric methods. In addition such observations and innovations in using these methods will here be mentioned as have been made by the writer in an experience of a year or so in analyzing the Mexican ores for the large exporters.

Only a limited number of commercial chemists both on this continent and in Europe are now engaged in doing this kind of work, because of the past wide variation in results frequently reported on the same sample, caused doubtless by the use of methods not so applicable to this class of ores, which is a matter of much importance considering the large shipments made from Mexico. The following list is of interest in showing the percentages of antimony reported on the same samples of Mexican ores by three prominent English commercial analysts before definite methods had been settled upon, and also the necessity for such a procedure. A, B, and C represent the results of these three chemists, B and C being of London, and D the percentage finally agreed upon in settling.

Sample No.	A.	B.	C.	D.
I	59.96	55.25	56.1	55.6
II	55.8	53.62	52.0	52.8
III	57.27	54.02	54.2	54.1
IV	58.13	54.5	54.8	54.6
V	60.78	59.23	63.1	60.0
VI	57.45	53.7	53.6	53.6
VII	....	53.5	54.4	53.9
VIII	59.8	53.2	54.9	53.5
IX	53.2	52.0	57.8	52.6
X	....	50.4	51.5	50.9
XI	....	52.4	53.7	53.0
XII	....	51.7	53.2	52.4
XIII	....	46.03	47.7	46.8

These ores are known to the trade as "clean ores," it being of rare occurrence to find impurities in the grades shipped other than silica, iron, and lime which obviously would not interfere with the schemes of analysis used. The metals of the fifth and sixth groups sometimes found accompanying antimony in ores, such as lead, mercury, copper, tin, and arsenic, when found in quantities larger than traces should be separated from the antimony when it is to be determined by the method used for sulphides, and also tin and arsenic when the antimony is to be determined by the oxide method. Shipments of ore from an unknown locality should consequently be put through a series of preliminary tests, and it is always advisable to test every sample for the most common impurities such as lead and arsenic; qualitatively for the purpose of modifying the sulphide method

and quantitatively if found in appreciable quantities, because of having to be taken into consideration in estimating the market value of the ore.

Lead is determined both qualitatively and quantitatively as the orange-yellow chromate ($PbCrO_4$). For the qualitative test the finely ground ore is boiled with concentrated nitric acid for several minutes, and, if a sulphide, until the sulphide of antimony is entirely converted into the insoluble white oxide, then cooled and diluted. Ammonia is added in excess, then acetic acid in excess, and the whole heated for several minutes in order to bring the lead salts thoroughly into solution. The insoluble matter is now filtered off, and the filtrate treated with an excess of potassium bichromate which precipitates the lead as chromate from this ammonium acetate and acetic acid solution. The lead can also advantageously be determined quantitatively in this form from the sulphide precipitate remaining on the filter after separating the antimony from the metals of the fifth group as will be explained later in the scheme of analysis.

For arsenic a combination of the Canby and Mohr methods is used. One gram of the finely powdered ore is mixed in a porcelain crucible with eight to ten parts of a mixture of equal parts of sodium carbonate and niter, gradually brought to fusion over a burner or in a muffle and kept so for five minutes or more. The fused mass is allowed to cool, disintegrated in hot water and the insoluble matter filtered off. The filtrate is now acidified with nitric acid and the carbonic and nitrous acid gases boiled off. An excess of an emulsion of zinc oxide, so apparent in the bottom of the beaker, is added, and should an unusually heavy precipitate of gelatinous silica and alumina be produced, a second filtration is necessary, also an extra addition of zinc oxide to the filtrate before the precipitation of the arsenic. This is precipitated as the reddish brown silver arsenate (Ag_3AsO_4) by the addition of silver nitrate in slight excess accompanied by vigorous stirring.

The precipitate mixed with zinc oxide is filtered, washed with cold water until the washings show no silver reaction, and dissolved off the filter with hot dilute nitric acid, catching the solution and washings in a beaker free from chlorine. When cold this is titrated for silver with an empirical solution of potassium

or ammonium thiocyanate using one cc. of a saturated solution of ferric sulphate as indicator, and titrating to the same pale amber-yellow color as was obtained in standardizing the solution against pure silver. For the standard silver solution one gram of the pure metal is dissolved in nitric acid, boiled to expel red fumes and diluted to 100 cc. For the standard thiocyanate solution nine and three-tenths grams of potassium thiocyanate or seven and six-tenths grams of ammonium thiocyanate are dissolved and diluted to one liter; then 1 cc. = 0.010 gram silver, and 108 silver = 25 arsenic. This same treatment somewhat modified is used in testing the ore qualitatively for arsenic. After fusion, the addition of acid, boiling and the addition of zinc oxide in excess, the whole is filtered and the neutral filtrate tested for arsenic as before.

The antimony ores of Mexico most common to the trade are those of stibnite (Sb_2S_3); cervantite (Sb_2O_4) produced by the oxidation of the former; oxysulphides, mixtures of these two with a preponderance of the former, and senarmontite (Sb_2O_3) which is, however, of much rarer occurrence. The composition of the oxide may be inferred from its behavior when boiled with concentrated hydrochloric acid with the subsequent addition near the end of the treatment of a few drops of nitric acid. Cervantite treated thus is but sparingly soluble, while senarmontite is almost if not completely so. Stibnite is also completely soluble; if, however, the ore be an oxysulphide as is frequently the case, insoluble oxide of antimony is found in the siliceous residue which is afterwards determined by fusion.

The following analysis of an ore from the state of Oaxaca illustrates this statement in regard to the solubility of these oxide ores: Moisture, 0.3; silica, 8.5; iron oxide and alumina, 1.6; iron pyrites (FeS_2), 0.9; lime and magnesia, traces; cervantite (Sb_2O_4), 3.8; senarmontite (Sb_2O_3), 84.7; total, 99.8. The results of a complete analysis being calculated to their probable composition, left a difference of 88.7 per cent., to be filled by the 70.8 per cent. soluble and the three per cent. insoluble antimony found, and which were calculated to the composition of senarmontite and cervantite as they were shown to be by their solubility.

Upon the behavior of these ores when treated with concentra-

ted hydrochloric acid plus a few drops of acid and boiling, is based their division into the following three classes for applying the schemes of analysis: 1. The soluble ores—stibnite (and senarmontite); 2. The practically insoluble ores—cervantite; 3. The partially soluble ores—the oxysulphides, stibnite mixed with cervantite.

1. *The Soluble Ores.*—For the "*soluble ores*" one gram, which has been finely pulverized in an agate mortar, is treated in a No. 3 beaker with twenty-five cc. concentrated hydrochloric acid, covered and boiled on a plate or over a flame until apparently decomposed and the solution is not more than fifteen cc. in bulk. About two grams of tartaric acid are added, and as soon as that is dissolved about four to six drops of concentrated nitric acid, and the whole is boiled for a minute or so more. This last addition causes a violent reaction and a more complete decomposition. The beaker is now removed from the source of heat, the cover and sides washed down, the insoluble residue filtered out and the filtrate and washings diluted in bulk to about 250 cc. A steady stream of hydrogen sulphide gas is now run through the solution for about an hour until it is thoroughly saturated and the antimony thus precipitated as the amorphous orange-colored sulphide (Sb_2S_3).

To insure a complete precipitation this is gently warmed in order to convert any basic chloride into sulphide and then allowed to stand an hour or so in the cold before filtering. The filtrate will then be perfectly clear and not deposit additional antimony upon standing or upon further treatment with hydrogen sulphide gas. Should lead or other impurities of the fifth group have been found by the preliminary qualitative tests, after filtering and washing the precipitate with cold water it is washed back into the beaker in which it was precipitated and treated with ammonium sulphide in such excess that with the aid of heat the antimony precipitate completely dissolves. The solution is then run back through the same filter, caught in a clean beaker and the filter thoroughly washed with hot water. The solution and washings are acidified in slight excess with hydrochloric acid, reprecipitating the antimony sulphide, diluted to about the same bulk as before (250 cc.), allowed to stand a few minutes to settle and then filtered. In the black sulphide

residue remaining on the filter representing the impurities of the fifth group, the lead may now be determined by placing the filter containing this precipitate into a beaker, treating with nitric acid and boiling, adding ammonia in excess, then acetic acid in excess, filtering, reprecipitating the lead as chromate and weighing it thus on a Gooch crucible or balanced filter-papers.

The antimony sulphide precipitate, whether precipitated but once or reprecipitated for purification, is now washed well upon a large, plaited, balanced filter with cold water and dried in an air-bath at 110° C. for two hours or more to constant weight. After removal and as soon as cold the weight of the dried precipitate is taken which consists of antimonous sulphide (Sb_2S_3) mixed with a small amount of free sulphur.

The following procedure has been found both rapid and accurate for weighing this precipitate. A German corrugated filter, 15 cm. in diameter, is used. Two are selected which lay beside one another in the same pack and which from long impact contain practically the same amount of moisture. They are balanced by cutting down the heavier one. Upon the unaltered one the precipitate is filtered, the other accompanying it in the drying oven and as a counterpoise in weighing. When the weight of the precipitate has thus been determined it is carefully scraped from the paper and powdered and mixed well by grinding in a small glass mortar. A certain amount of this (five-tenths gram) is weighed off into a platinum boat, this introduced into a glass combustion tube and the free sulphur driven off in a stream of carbon dioxide. From the weight of the resulting black anhydrous antimonous sulphide so obtained on a weighed amount of the dried precipitate, its total weight thus treated can easily be calculated, and it is then simply a matter of calculation to determine the total amount of antimony present. $Sb_2S_3 \times 0.7177 = Sb$.

The combustion requires in all from twelve to fifteen minutes, and if carefully conducted with the following precaution, very little loss if any at all occurs. Arsenic if present would be volatilized. (*a*) A steady stream of gas should be passing through the tube when the flame is applied underneath the boat, and should continue so with as little variation as possible until the end of the operation. Should this not be the case, a flame

would at first play over the surface of the contents of the boat causing oxidation apparent to the eye when removed from the tube by a whitening of the surface and consequently a loss in weight. (*b*) The heating of the boat in the tube should be accomplished gradually. At first a gentle heat is applied until all the sulphur has apparently been driven off, and increased towards the end of the operation. (*c*) The tube should be cleaned of sublimed sulphur by heating before each and every determination. After weighing the boat and contents it is well to treat again for additional loss in weight, which is rarely found if the operation has been conducted as described.

2. *The Practically Insoluble Ores.*—The important point here is the decomposition of the ore which is accomplished by fusion. One gram of the finely powdered ore is mixed with eight to ten parts of a flux composed of equal parts of flowers of sulphur and sodium carbonate, introduced into a porcelain crucible (capacity forty cc.), and in addition the mixture is covered with a thin layer of the flux. The covered crucible is introduced into the opening of a muffle that is of a bright red heat and is cautiously heated to fusion for about ten minutes. The heat applied at first should be of such an intensity that sulphur flames are barely seen escaping around the edge of the lid; after they cease it is somewhat increased by pushing the crucible a few inches farther back in the muffle. At no time should the crucible become heated to more than perceptible incandescence on the side facing the source of heat, and during the operation it should be occasionally turned with a pair of tongs to insure an even heating and consequently a complete decomposition. The color of the melt when cold should be green, not yellow, and likewise the solution of the same due to the sulphide of iron present. A suggestion of a yellow color particularly in the solution indicates an incomplete decomposition of the ore, and but a partial change of the antimony into the soluble sodium sulphantimonate which consequently necessitates a repetition of the fusion.

A successful fusion owing to the ready volatility of antimony at a comparatively low degree of heat is rather a delicate thing and difficult to accomplish, requiring constant care and judgment only gained by experience. With the statement that it is possible to thoroughly decompose such an ore by fusing over a

candle flame, the writer is compelled to differ, having frequently found that a fusion made at a seemingly alarming degree of heat gave when dissolved a yellow solution in which the antimony when determined was found to be lower than that of a duplicate sample which had been treated to a higher degree of heat. It is, therefore, better to treat in excess than not to fuse enough; for should there be a slight loss by volatilization, this would in a measure be counterbalanced by the small amount of impurities, such as silica, obtained from the action of the flux on the crucible and on the silica of the ore, and consequently thrown down by the acid and weighed with the antimony sulphide precipitate. The degree of heat used, however, should scarcely effect the glaze of the crucible. When the fusion has thus been satisfactorily accomplished and when cool, it is dissolved in hot water, which takes but a few minutes, thes uspended precipitate of iron sulphide and sulphides of the metals of the fourth group, if present, filtered off, and the antimony precipitated by adding a slight excess of hydrochloric acid to the filtrate. After stirring and allowing to stand a few minutes to settle the precipitated antimonic sulphide (Sb_2S_5), mixed with more or less free sulphur, is filtered off upon a balanced filter and so determined as before, being ultimately weighed when removed from the combustion tube as antimonous sulphide (Sb_2S_3).

3. *The Partially Soluble Ores.*—These ores require a double treatment, that is they are first treated as for soluble ores and the antimony determined in the acid solution, and the residue, remaining on the filter which contains the undissolved oxide, is subjected to a fusion as for oxide ores. This filter-paper is placed in the bottom of a porcelain crucible and covered well with flux so that some comes in direct contact with its contents. It is then fused as directed. In dissolving, pieces of charred paper may possibly be found, which are, however, filtered out together with the insoluble matter. The amount of antimony so present is determined as before.

Most Mexican so-called sulphide ores exported are really oxy-sulphides being mixtures of sulphide with a small amount of oxide which has not been separated in the sorting; these ores consequently require this double treatment. The following is a list of results obtained in using these methods upon the pre-

viously mentioned varieties of Mexican ores, and gives in the case of oxysulphides the soluble and insoluble antimony found. In the last column will also be found the results by the fire assay, which is extensively used on oxide ores for prospecting work, and also for large shipments when the "wet assay" is to be made later at their destination. It is figured by the dealers that the wet assay of a sixty per cent. ore will go six per cent. higher than the dry or fire assay. That there are exceptions to this will be seen in Nos. 5, 8, and 12 of the table. No. 5 is the senarmontite ore, the complete analysis of which has already been given, while Nos. 8 and 12 are quite insoluble under the acid treatment leading to the supposition that they are cervantite ores of the composition Sb_2O_4. It has also been observed that certain grades of oxide ores give higher results by fire assay than other grades, which is considered due to their ultimate composition of which very little is so far known. The widely different and extremely low results obtained by fire assay upon sulphide ores makes them no criterion upon which to judge of the actual antimony present, and so for this class of ores it is falling into disuse.

No.	Class of ore.	Soluble Sb.	Insoluble Sb.	Total Sb.	Fire assay.
1.	Sulphide	67.4	..	67.4	....
2.	"	28.5	..	28.5	....
3.	Oxysulphide ...	61.6	5.1	66.7	48.0
4.	" ...	63.3	6.7	70.0	45.0
5.	Oxide	70.7	3.1	73.8	72.8
6.	"	...	..	71.7	65.0
7.	"	...	..	66.1	59.0
8.	"	...	..	63.9	61.8
9.	"	...	..	55.8	49.0
10.	"	...	..	49.0	43.0
11.	"	...	..	48.3	43.0
12.	"	...	..	46.4	44.4

The fire assay referred to consists of the reduction of the contents of the ore to the metallic state by fusion with potassium cyanide and while it is known that it is possible to obtain higher results by the use of other mixed fluxes together with a treatment for a longer time at a lower heat, this cyanide reduction remains the accepted method in trade. It is performed as follows: Five grams of the powdered ore is mixed with twelve

parts of potassium cyanide, placed in a ten gram clay crucible and covered with salt. The fusion is made in a muffle at a bright red heat, allowing it to remain there thirteen minutes. When removed it is thoroughly shaken to collect the globules into one metallic button and allowed to cool. The crucible is broken and the resulting button carefully broken from the slag and weighed.

In conclusion the writer desires to express his obligation both to Mr. M. Elsasser and to Mr. Ferdinand McCann for their kind assistance in furnishing him with suggestions, data, etc., without which this paper would not have been written.

LABORATORY OF HECKLEMANN AND MCCANN,
CITY OF MEXICO.

ELECTROLYTIC DETERMINATION OF ZINC IN THE PRESENCE OF MANGANESE.

BY EMIL J. RIEDERER.

Received May 23, 1899.

IN determining zinc quantitatively by means of the electric current, it is essential to have the zinc in the form of sulphate and there should be neither nitrates nor chlorides present.

It was found best to use a platinum dish, on which silver had been deposited, for a cathode. In the first experiments, I tried copper deposits on platinum, but discarded this owing to the fact that copper is too easily oxidized, and consequently causes variation in weight. During the deposition of zinc it is found best to stir the solution (using a mechanical stirrer) continually, so as to obtain an even and uniform deposit; and to keep the temperature under 26° Celsius.

The current used for the deposition of zinc was four volts, giving a current of three and five-tenths volts and 0.20 to 0.26 amperes for 100 sq. cm. of cathode area. The current may vary from 0.20 to 0.26 amperes and the temperature from 15° to 26° Celsius.

Different proportions of zinc and manganese were tried so as to determine the action of the manganese, but in no case could any traces of manganese be found in the zinc which was deposited on the cathode.

The following reagents were used for the electrolysis:

a. A solution of lactic acid ($CH_3.CHOH.COOH$, each

cubic centimeter of which contained 0.937 gram of lactic acid.

b. A solution of ammonium lactate ($CH_3.CHOH.COONH_4$) each cubic centimeter of which contained 0.50 gram of ammonium lactate.

c. Ammonium sulphate, $(NH_4)_2SO_4$, crystalline.

The volume of the solution in all cases was 230 cc.; the cathode surface 150 sq. cm., and the anode one and one-half cm. distant from the cathode.

The zinc and manganese salts used were the sulphates $ZnSO_4.7H_2O$ and $MnSO_4.7H_2O$.

ANALYSIS NO. 1.

Zinc sulphate	0.5074 gram
Manganese sulphate	0.1634 "
Ammonium lactate	5.0000 "
Lactic acid	0.7500 "
Ammonium sulphate	2.0000 "
Ampere, varying from	0.24-0.26 $N.D._{100}$
Voltage, " "	3.7–3.9
Temperature varying from	20°–25° C
Percentage of zinc found	22.786
" " " theory	22.78
Time required to deposit zinc completely	4 hours, 10 minutes

No traces of manganese were found in the zinc.

ANALYSIS NO. 2.

Zinc sulphate	0.5000 gram
Manganese sulphate	0.4466 "
Ammonium lactate	5.0000 "
Lactic acid	0.7500 "
Ammonium sulphate	2.0000 "
Ampere varying from	0.2–0.22 $N.D._{100}$
Voltage " "	3.5–3.8
Temperature varying from	15°–22° C.
Percentage of zinc found	22.82
" " " theory	22.78
Time required to deposit zinc completely	4 hours, 10 minutes.

ANALYSIS NO. 3.

Zinc sulphate	0.5000 gram
Manganese sulphate	2.0000 "
Ammonium lactate	5.0000 "
Lactic acid	0.3800 "
Ammonium sulphate	2.000 "
Ampere varying from	0.2–0.23 $N.D._{100}$
Voltage " "	3.0–3.6
Temperature varying from	18°–24° Celsius
Percentage of zinc found	22.72
" " " theory	22.78
Time required to deposit zinc completely	$5\frac{1}{2}$ hours

In all I have made about sixteen separations of zinc from manganese in the manner described, but in only two cases did the electrolysis require more than five and one-half hours, or did the result vary more than 0.10 per cent. from the theoretical value. Constant stirring was found to give a more rapid and uniform silver-like deposit of zinc.

In several cases manganese hydroxide was found on the anode, in small amounts during the electrolysis, but in no case could any traces of manganese be found in the deposited zinc.

During every electrolysis containing manganese, it was noticed that the solution turned from colorless to amethystine, the more manganese present the darker the color. On allowing this solution to stand for a short while, after having removed it from the platinum dish, and disconnected the current, it was noticed that the solution again became colorless.

It was found that the best results were obtained between the temperatures of 15° and 28°C. If below 15° C. the electrolysis requires longer, if above 28° C. the zinc may deposit in such a manner (either large crystals or even spongy) as might cause loss in washing. The amount of zinc deposited in each electrolysis should not be more than 0.1700 gram of pure zinc.

After the electrolysis is completed the solution is poured off, the zinc deposit washed with distilled water, alcohol, and finally with pure ether to remove alcohol; then place a in the hot water oven to dry perfectly, then placed in a desiccator until ready for weighing. This washing and drying should not require more than five minutes.

When an electrolysis is started the current should be regulated to 0.25 ampere $N.D._{100}$, and if the temperature is between 15° and 28° C. it will be found that during the entire process the current will vary but slightly.

If the current is increased to more than 0.30 ampere $N.D._{100}$ (normal density of current for 100 sq. cm. of cathode area) it is found that the zinc will not be deposited evenly, and more manganese hydroxide will be found at the anode ; also that the zinc being deposited so quickly, and in larger crystals, will mechanically enclose some manganese or solution. If the current is less than 0.20 ampere $N.D._{100}$ the time required for complete deposition will be longer.

The solution from which zinc is to be deposited should always be neutral or slightly acid.

These experiments were made during 1897–1898 in the laboratory of the Koeniglichem Polytechnikum in Munich, Germany.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 40.]

THE INFLUENCE OF SUBSTITUENTS ON THE ELECTRICAL CONDUCTIVITY OF BENZOIC ACID.[1]

BY ALFRED TINGLE.

Received July 14, 1899.

INTRODUCTORY.

VICTOR MEYER and his pupils have shown that in a substituted aromatic acid, the rate of esterification is affected by the nature and position of the substituting atoms or groups. Kellas[2] proved that for monochlor-, monobrom-, and moniodobenzoic acids, the rate of esterification varies with the molecular weight of the acid, or in other words, with the atomic weight of the substituting halogen. Thus, graphically represented, when the molecular weight of the acid is taken as the abscissa, and the percentage of ester formed in a given time, as the ordinate, a straight line is obtained.

No attempt appears to have been made, even in view of this work, to examine the effect of the position and nature of a substituent on the electrical conductivity of the aromatic acids. The conductivities of substituted benzoic acids have been examined by many investigators, but usually with the view of determining their affinity coefficients, and with little regard for the nature of the substituting group.

The conductivities of salts of organic acids have also been investigated, notably by Ostwald, but never, as it would appear, with the view of finding any relation between the conductivities in question and the atomic weights of the metals forming these salts.

The present investigation was undertaken with the object of examining into the changes introduced in the conductivity of benzoic acid, by the substitution of various metals for the

[1] From author's thesis for the Ph.D. degree.

[2] Kellas: Inaugural Dissertation, Heidelberg, 1897.

hydrogen of the carboxyl group, and of halogens for the hydrogen of the benzene nucleus.

It was hoped that these substituting elements might be found to have an influence traceable to their position in the periodic table. It was further thought possible that some definite relationship might be disclosed between the conductivities of position-isomers.

With these objects in view, the elements substituting carboxylic hydrogen were entirely selected from Group I of the periodic table, while those entering the nucleus in the two chosen positions ortho and para were from Group VII.

We are thus in a position to see:

1. What is the effect on its electrical conductivity of introducing an alkali metal into the carboxyl group of benzoic acid, and how this effect varies with the atomic weight of the metal.

2. What effect is produced on its electrical conductivity when, in a salt so formed, a hydrogen atom is replaced in the ortho, or in the para position, by one of the heavier halogen atoms.

The work described in the pages which follow is of a purely preliminary nature, and no claim to extreme accuracy is made.

Several factors militate against any such claim, notably the small quantities of substance available in some cases, with a consequent absence of certainty that purification was thorough. Another objection, which may plausibly be made, is that the conductivity of the water employed was comparatively high, so rendering the correction to be applied somewhat uncertain.

Nevertheless it is believed that the approach to accuracy is sufficiently near to show certain points which merit further investigation. Some idea as to this degree of accuracy may be gained by noting the extent of agreement, where, for any reason, determinations of conductivity have been made from separately prepared samples of the same compound.

Perhaps it should be noted that many of the salts studied in this research have not hitherto been elsewhere described.

PRACTICAL.

Preparation of p-Brombenzoic Acid.—Commercial toluene was brominated in the usual manner. The resulting product was

repeatedly fractionated, those portions passing over between 130° and 190° being collected. The bromtoluene so obtained was heated with an excess of nitric acid (one part concentrated acid to three parts water) till oxidation to the corresponding acid was complete. The crystals which separated, on cooling, from a large volume of the acid liquid were found to have the melting-point 248° (melting-point of *p*-brombenzoic acid, 251°). They were purified by repeated extraction with hot water, and were finally recrystallized from alcohol till they possessed the constant melting-point of 251°–252°.

Preparation of o-Brombenzoic Acid.[1]—This acid was obtained from *o*-amidobenzoic acid by the Sandmeyer reaction. The crude product was repeatedly crystallized from water, converted into its barium salt, reobtained by treating this with hydrochloric acid, and finally crystallized from dilute alcohol until it possessed a constant melting-point.

Preparation of p-Iodobenzoic Acid.—*p*-Iodobenzoic acid was obtained by the oxidation of *p*-iodotoluene. Chromium trioxide and glacial acetic acid were at first used for this purpose; it was subsequently found that boiling with dilute nitric acid was a much preferable means of procedure. By the latter method the oxidation seems to be quite as rapid and as readily controlled. It is also much easier to obtain the product in a pure form. The products obtained by the above two methods were mixed together and carefully sublimed. The acid was then further purified by crystallization from slightly dilute alcohol; it then had the melting-point 267°–268°.

Preparation of o-Iodobenzoic Acid.—This was obtained by two processes. A part of the acid employed was made by oxidizing *o*-iodotoluene with boiling dilute nitric acid. This seems to be the best method, even the crude product being very nearly pure. It was necessary, however, to obtain the greater part of the acid used in these experiments from *o*-amidobenzoic acid by the Griess reaction. The acid obtained in this way was purified by repeated crystallization from hot water, till it possessed the correct melting-point. It was mixed with the portion of acid obtained by oxidizing *o*-iodotoluene, and the whole was then twice recrystallized.

[1] For the preparation of this and of the similarly obtained *o*-iodobenzoic acid, I am indebted to my fellow-student, Mr. T. M. Taylor.

Purification of Benzoic Acid.—"Chemically pure" benzoic acid was dissolved in hot water, the solution filtered, and allowed to crystallize. The product was again crystallized from water, when its melting-point remained unaltered and correct.

Preparation of Pure Water.—The method adopted was a slight modification of that suggested by H. C. Jones and Mackay.[1] The only change made, at first, was that of substituting a well-steamed hard glass condenser for the block-tin condenser employed by these workers. The water so obtained was, of course, inferior in purity to that obtained by them, but was considered to be sufficiently pure in view of certain other sources of error. It was of fairly uniform quality, the average conductivity being 4.4×10^{-6} mercury units. In every case a correction has been applied, based upon a determination of the particular sample of water employed. It was later found that much time could be saved by refilling the washing retort, after each occasion on which the apparatus was cleaned, with an alkaline solution made from previously purified water. In this way it was possible to dispense with the use of potassium permanganate in the washing retort without the least danger of ammonia passing over, even in the first portions.

Method of Operation.—These conductivities were determined, by the method of Kohlrausch, at a temperature of 25°. The resistance capacity of the electrode vessel was found by using a solution of pure potassium chloride.

The bridge wire was one meter in length, and was not calibrated. In making up the solutions to be determined, a calculated quantity of the salt, dried at 120°–130°, was accurately weighed out, dissolved in water, and the solution brought up to the proper volume. Except where otherwise stated, the solution so obtained was $\frac{n}{64}$, the solution $\frac{n}{128}$ being generally prepared by diluting the stronger solution in the electrode vessel.

SALTS OF *p*-IODOBENZOIC ACID.

The method by which these salts were prepared is typical of that employed with all except the benzoates. The dry alkaline carbonates were accurately weighed and dissolved in water. To these solutions a calculated quantity of *p*-iodobenzoic acid was

[1] *Am. Chem. J.*, **19**, 90.

added. The quantity of acid employed was about five-tenths milligram more than was necessary exactly to neutralize the alkali; it was considered impossible on account of adherent moisture, etc., to weigh out exact equivalents of acid and carbonate, but more easy to afterwards remove this slight excess of acid than a possibly unforeseen trace of alkali. The mixture so obtained was warmed on the water-bath till no further reaction could be observed to take place. It was then cooled and filtered (the acid being almost insoluble in cold water). The clear solution so obtained was evaporated to dryness on the water-bath, and the residue then crystallized from its most convenient solvent. The salt was next air dried, and finally dried at 120°–130° as mentioned above.

Sodium p-Iodobenzoate.—This salt crystallized from water in needles.

Conductivity determination:

v	μ
64	66.04
128	67.39

Potassium p-Iodobenzoate.—The salt employed was crystallized from alcohol, and the crystals very thoroughly washed with ether.

Conductivity determination:

v	μ
64	74.66
128	77.05

Rubidium p-Iodobenzoate.—This salt crystallized in beautiful plates and needles from a mixture of alcohol and ether.[1]

Conductivity determination:

v	μ
64	93.53
128	97.19

Cesium p-Iodobenzoate.—Crystallized from alcohol and ether, in needles.

[1] A mixture of alcohol and ether is not commonly employed, it is believed, in the crystallization of the alkali salts of organic acids. In the course of this work it has been frequently used with the best results, giving good, and very pure crystals. By the use of this solvent the waste incidental to recrystallizations was reduced to a minimum, while it was eminently calculated to remove any trace of acid. The method of handling the medium is to dissolve the salt in a little hot alcohol, allow this to cool somewhat, and add about five times its volume of ether.

Conductivity determination:

v	μ
64	88.18
128	90.48

SALTS OF *p*-BROMBENZOIC ACID.

The general method employed in preparing these salts was identical with that given under the salts of *p*-iodobenzoic acid.

Sodium p-Brombenzoate.—This salt did not readily crystallize from water. It was purified by the use of alcohol. In this medium it dissolved with some difficulty, separating when cool as a gelatinous precipitate, which dried to a somewhat horn-like mass.

Conductivity determination:

v	μ
64	65.14
128	67.10

Potassium p-Brombenzoate.—Crystallized from alcohol, in large plates somewhat resembling mica in general appearance. The crystals were washed first with a little alcohol, and then with much ether. In this case the two solutions employed were prepared independently, and from samples of the salt made at different times.

Conductivity determination:

v	μ
64	86.74
128	87.58

Rubidium p-Brombenzoate.—Crystallized from a mixture of ether and alcohol, in needles.

Conductivity determination:

v	μ
64	86.21
128	88.93

Cesium p-Brombenzoate.—Crystallized in needles, from a mixture of ether and alcohol.

Conductivity determination:

v	μ
64	83.71
128	88.03

SALTS OF *o*-IODOBENZOIC ACID.

The method applied to the preparation of the foregoing salts was also used here. The greater solubility of the ortho acid, however, made it necessary to use a small quantity of water in the first stages of these preparations.

Sodium o-Iodobenzoate.—Crystallized from alcohol-ether mixture.

Conductivity determination:

v	μ
64	64.21
128	67.35

Potassium o-Iodobenzoate.—Crystallized from alcohol-ether mixture.

Conductivity determination:

v	μ
64	78.94
128	83.36

SALTS OF *o*-BROMBENZOIC ACID.

The remarks on the preparation of *o*-iodobenzoates apply equally to these salts.

Sodium o-Brombenzoate.—Crystallized in magnificent feathery needles from a mixture of ether and alcohol. The two solutions ($v = 64$ and $v = 128$) employed were from different samples of the salt, and were made independently of one another.

Conductivity determination:

v	μ
64	66.11
128	68.02

Potassium o-Brombenzoate.—The purification of this salt offered some slight difficulty on account of its great solubility and the small quantity available for the work. It refused to crystallize from alcohol, with which it formed a somewhat oily solution. On the addition of ether to this, the ether quickly separated as a distinct layer, and failed to induce crystallization. The whole was therefore evaporated to dryness, and the dry salt so obtained quickly washed on the filter with a mixture of ether and a little alcohol.

Conductivity determination:

v	μ
64	86.92
128	90.92

SALTS OF BENZOIC ACID.

In preparing the benzoates in pure condition, the comparatively great solubility of benzoic acid offered a difficulty. This was, it is believed, overcome by prolonged gentle heating of the aqueous solutions on the water-bath, and the use of considerable volumes of alcohol in the later crystallizations.

Lithium Benzoate.—In this case advantage was taken of the comparative insolubility of lithium carbonate: this was weighed out in slightly greater quantity than that calculated for the previously weighed benzoic acid. The two were mixed in the presence of alcohol and warmed. On the reaction ceasing, the excess of lithium carbonate was filtered out, the solution evaporated to dryness and the residue dissolved in a little water. The solution was again filtered, and again evaporated to dryness. The salt was finally crystallized from a mixture of alcohol and ether.

Conductivity determination:

v	μ
64	57.30
128	59.67

Sodium Benzoate.—This salt did not crystallize at all well from water, but merely dried out on the sides of the beaker. It showed little tendency to dissolve in alcohol, and from this medium it was deposited in gelatinous form. The attempt at crystallization was therefore abandoned; the salt solution was evaporated to dryness, the solid mass repeatedly extracted with hot alcohol, and finally washed on the filter by the same liquid. From the foregoing it is evident that the purity of this sample of the salt must remain doubtful.

Conductivity determination:

v	μ
64	67.93
128	70.66

Potassium Benzoate.—This salt was crystallized from alcohol, in which it is very soluble, and was subsequently washed with ether.

Conductivity determination:

v	μ
64	88.05
128	92.02

Rubidium Benzoate.—The salt is readily soluble in hot, but rather insoluble in cold, water, a property which rendered it all the more difficult to remove benzoic acid; in this case, therefore, the steaming of the salt on the water-bath was prolonged. It was ultimately crystallized from a mixture of ether and alcohol. From this medium it deposited in beautiful plates, but from water it appeared in the form of needles. Two preparations were made and their conductivities determined separately.

Conductivity determination:

v	μ
64	92.04 (1st preparation)
64	91.48 (2d ")
128	94.33 (3d ")

Cesium Benzoate.—This salt appears to be more soluble in cold water than the foregoing. It was crystallized from alcohol and ether. The two solutions employed were made independently, from different samples of the salt.

Conductivity determination:

v	μ
64	91.85
128	94.66

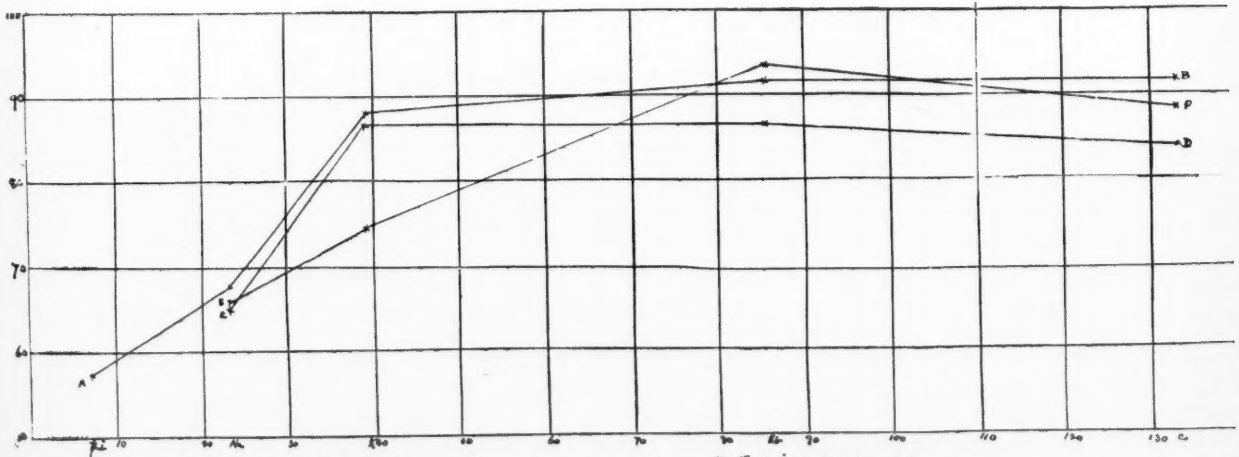
An attempt was made to determine the conductivity of lithium *p*-brombenzoate. The pure salt was obtained in solid form with difficulty, as it is very soluble in alcohol and appears to be somewhat soluble even in ether alone. On being placed between filter-paper and left over night, the crystals deliquesced completely. No further preparation of the salt was made. Lithium *o*-iodobenzoate was also prepared. It was obtained as a gummy mass, which, on long standing, became permeated with stellate groups of needles. On the addition of ether it immediately reassumed its original gummy form, and the attempt to purify it was abandoned.

CONCLUSION.

Ostwald[1] has experimentally shown, in a large number of cases, that where two metals form salts with the same acids, the

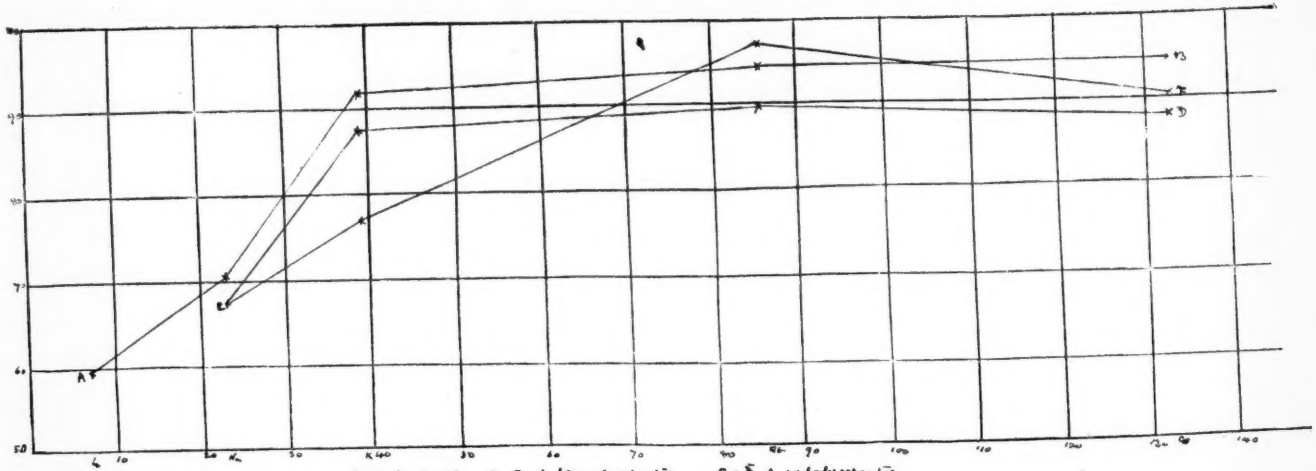
[1] *Ztschr. phys. Chem.*, 1, 74 and subsequent papers.

I v. 64.



A-B benzoesäure C-D p. brombenzoesäure E-F p. iodobenzoesäure.

II $v = 128$.



A-B długości C-D ↓ krawędziowości E-F ↓ wydłużenia.

difference in conductivity of the same salts of the two metals is constant, and independent of the nature of the acids. He has also pointed out that this phenomenon is directly deducible from Kohlrausch's law of conductivity. A glance at the appended table of conductivities ($v = 64$), obtained in this research, will show that the variations from this rule are very marked in some cases, and are far in excess of what is believed to be the experimental error.

A graphic representation of the same table is given on Plate I, while Plate II shows the results when $v = 128$. The ordinates represent μ, and the abscissae the atomic weight of the metal. According to the law previously referred to, the curves, whatever their form, should be parallel, or at least approximately so, a condition which these do not fulfil.

In view of these variations, it seems necessary to refrain, for the present, from any attempt to draw theoretical conclusions from the results obtained. They are not final, but show that this series of salts requires further investigation. Perhaps, however, it may be allowable to point out that the departure from theory is much greater in the case of the potassium and sodium iodobenzoates than in those salts which the same metals form with acids of smaller molecular weight.

TABLE OF CONDUCTIVITIES.

($v = 64$.)

Salts of *p*-iodobenzoic acid.			Salts of *p*-brombenzoic acid.		
Metal.	μ.	Difference.	Metal.	μ.	Difference.
Cs.....	88.18		Cs.....	83.71	
		5.35			2.50
Rb	93.53		Rb	86.21	
		18.87			0.53
K	74.66		K	86.74	
		8.6			21.60
Na.	66.04		Na	65.14	

Salts of benzoic acid.			Salts of *o*-iodobenzoic acid.		
Metal.	μ.	Difference	Metal.	μ.	Difference.
Cs.....	91.85		K	78.94	
		0.99			14.73
Rb	91.76		Na	64.21	
		3.71			
K	88.05		Salts of *o*-brombenzoic acid.		
		20.12	Metal.	μ.	Difference.
Na	67.93		K	86.92	
		10.63			20.81
Li.....	57.30		Na	66.11	

NEW BOOKS.

A DIGEST OF METABOLISM EXPERIMENTS IN WHICH THE BALANCE OF INCOME AND OUTGO WAS DETERMINED. BY W. O. ATWATER, PH.D., AND C. F. LANGWORTHY, PH.D. Bulletin No. 45 (Revised Edition). Washington : U. S. Department of Agriculture, Office of Experiment Stations. 434 pp.

This publication is a digest of about 3,600 experiments in which the balance of one or more of the factors of income and outgo was determined. It includes metabolism in both man and animals. The compilation has been prepared in connection with the work of the Office of Experiment Stations and, particularly, in connection with the investigations that are being pursued under the direction of Prof. Atwater, who is the special agent in charge of nutrition investigations. The compilation includes records, from the Russian literature and other sources, not found in general treatises and standard abstract journals. While the authors do not claim to have found all the investigations ever reported, they believe that comparatively few have escaped their attention.

An introductory chapter, containing a brief description of the compilation and a historical account of the subject, is followed by the experiments with man. These occupy three-fifths of the entire volume. Beginning with the nitrogen balance in healthy subjects, experiments on the influence of diet are first recorded, followed by those on the influence of other conditions. The experiments are numbered seriatim throughout the compilation. Each subject is treated separately. A table containing the data of the experiments is followed by a brief description of the objects and conclusions of each, together with other important information contained in the original publications.

After nitrogen metabolism in health are experiments on subjects in disease, arranged according to the classification of diseases in Osler's "Practice of Medicine." The experiments with man conclude with a description of those in which the balance of nitrogen and carbon was determined. In recording the experiments on animals, those on each animal are given collectively. At the end of the volume the names of experimenters and subjects are indexed separately.

The work shows that the literature has been extensively con-

sulted in its preparation and that this has been done with a thoroughness and intelligence essential to a valuable compilation of this kind. The arrangement of such material is difficult. While that presented in this volume has the disadvantage of separating some experiments that have a common interest, it appears to combine the greatest number of desirable qualities. The matter relating to each subject is well brought together in the index. E. E. SMITH.

THE ARITHMETIC OF CHEMISTRY. BY JOHN WADDELL. New York: The Macmillan Co. 1899. viii + 133 pp. Price, 90 cents.

This is the best elementary text-book upon chemical arithmetic, or stoichiometry, we have yet examined. The general mistake made by most books of this class is to attempt too much and to explain too little. Formulas and rules are used too frequently, and too many problems are to be solved by simply substituting for *a* or *b* its numerical value. In Mr. Waddell's book the explanations are clear, and the laws upon which the solutions of the problems depend are plainly stated. The ground covered by the book is not extensive, but the most important chemical problems, such as the calculation of weights, the solution of chemical equations, the volume of gases, the calculations in volumetric analysis, the deduction of formulas from percentage composition, etc., receive a generous share of attention. Among the examples given for solution are many selected from the examination questions of the leading American and British colleges. RICHARD K. MEADE.

BOOKS RECEIVED.

Bulletin No. 18. Sugar Beet Investigations in 1898. 24 pp. Bulletin No. 19. Miscellaneous Analyses (strawberries, peas, wines, foods, poisons, fertilizers, and potable waters). 24 pp. University of Idaho Agricultural Experiment Station, Moscow, Idaho. 1899.

A Short History of the Progress of Scientific Chemistry in Our Own Times. By William A. Tilden. London, New York, and Bombay: Longmans, Green & Co. 1899. x+276 pp. Price, $1.50.

Die aetherischen Oele. Von E. Gildemeister und Fr. Hoffmann. Bearbeitet im Auftrage der Firma Schimmel & Co. in Leipzig. Mit vier Karten und zahlreichen Abbildungen. Berlin: Verlag von Julius Springer. 1899.

Report on Investigations to Determine the Cause of Unhealthy Conditions of the Spruce and Pine from 1880–1893. By A. D. Hopkins. 265 pp.

Commercial Fertilizers. By B. H. Hite and T. F. Watson. 12 pp. The Effect of Pressure in the Preservation of Milk. By B. H. Hite. 34 pp. West Virginia Agricultural Experiment Station, Morgantown, W. Va.

On the Associated Minerals of Rhodolite. By W. E. Hidden and J. H. Pratt. 6 pp. On the Occurrence, Origin, and Chemical Composition of Chromite. By J. H. Pratt. 6 pp. Reprinted from the *American Journal of Science.*

La Liquéfaction des Gaz. Méthods Nouvelles—Applications. Par J. Cauro. Paris: Gauthier-Villars, Imprimeur-Libraire. 1899. 83 pp.

School Chemistry. By Charles Baskerville, Ph.D., of the University of North Carolina. Richmond, Va.: B. F. Johnson Publishing Co. 1899. 159 pp. Price, 60 cents.

Easy Experiments of Organic Chemistry for Students' Laboratory Work. By John Howard Appleton. Providence, R. I.: Snow & Farnham. 1898. 107 pp. Price, 60 cents.

Saw Palmetto. By P. L. Sherman and C. H. Briggs. Reprinted from the *Pharmaceutical Archives*, 2, No. 6. 16 pp.

Commercial Fertilizers. Bulletin No. 82, Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. 20 pp.

Alkali Studies, IV. By E. E. Slosson. Published as part of the Ninth Annual Report of the Wyoming Agricultural Experiment Station. July, 1899. Laramie, Wis. 29 pp.